STRUCTURE AND REACTIVITY OF COPPER DIPYRIDYL CARBINOL- AND RHENIUM DIPHOSPHINE COMPLEXES

Thesis by

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ABSTRACT

Two series of terphenyl-based ligands were designed and synthesized, and the reactivity of their transition metal complexes was examined in the context of small molecule activation.

Ligands bearing pyridyl donors and pendant hydroxyl groups were synthesized in order to accommodate multiple copper centers with varying steric environments. Copper(I) complexes of these ligands were prepared and characterized, in which copper is coordinated only via the pyridyl nitrogen donors. Treatment of the Cu(I) species with O_2 or deprotonation of the ligand followed by metallation with Cu(II) generates multinuclear copper cores supported by bridging alkoxides. Mono-, di-, tetra-, and hexanuclear copper complexes have been synthesized by changing the protonation state and backbone geometry of the ligand. The resulting copper complexes have been characterized by a variety of techniques including single-crystal X-ray diffraction and ^{1}H NMR spectroscopy.

Rhenium(I) carbonyl coordination chemistry was explored using a series of terphenyl diphosphine ligands with varying steric properties and substituents. Structural differences between complexes of the meta and para ligand variants have been characterized by single crystal X-ray diffraction and ^{31}P-NMR spectroscopy. Cyclic voltammetry studies reveal differences in redox properties, though neither complex appears to exhibit catalytic activity under CO_2. Subsequently, we investigate the chemistry of rhenium complexes of 2-methoxy-5-*tert*-butyl- or 2-methoxy-5-dimethylamino modified ligands.

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LIST OF ABBREVIATIONS

bipy	2,2'-bipyridine
CD_3CN	deuterated acetonitrile
$CDCl_3$	deuterated chloroform
CH_2Cl_2	dichloromethane
CV	cyclic voltammetry
DFT	density functional theory
dmb	4,4'-dimethyl-2,2'-bipyridine
DMF	dimethylformamide
DPK	di(2-pyridyl) ketone
dppe	1,2-bis(diphenylphosphino)ethane
EPR	electron paramagnetic resonance
Et_2O	diethyl ether
EtOH	ethanol
H_2O_2	hydrogen peroxide
IR	infrared
MeCl	chloromethane
$N(Me)_2$	dimethylamino
NaHMDS	sodium bis(trimethylsilyl)amide
NMR	Nuclear magnetic resonance
OMe	methoxy
OTf^-	trifluoromethane sulfonate
SCE	saturated calomel electrode
SHE	standard hydrogen electrode
TBAP	tetrabutyl ammonium perchlorate
t-Bu	*tert*-butyl
t-BuLi	*tert*-butyl lithium
THF	tetrahydrofuran
UV	ultraviolet
VT	variable temperature
XRD	X-ray diffraction
XylO	α,α'-bis[N,N-bis(2-pyridylethyl)amino]-m-xylene-2-olate

C h a p t e r 1

Synthesis, Structures, and Characterization of Multicopper Complexes Supported by Dipyridylcarbinol Ligands

Introduction

The study of structure, assembly, and properties of multimetallic complexes is important for a variety of reasons, from device applications (i.e., sensors[1], small-molecule magnets[2], etc.) to catalysts[3] to furthering basic knowledge in bioinorganic chemistry.[4] The ability of several metal centers to react cooperatively is unique to such assemblies, and holds great promise. However, it is difficult to predict and control the core structures of such assemblies as they are highly dependent on ligand and metal geometry, solvent and counterion effects, and oxidation state of the metals.[5, 35]

Biological systems extensively employ multimetallic clusters; examples include iron-sulfur clusters in ferrodoxins or nitrogenases, [FeFe] or [FeNi] clusters in hydrogenases, and di- or tricopper centers in oxidase and oxygenase enzymes.[6] Many of these metalloenzymes perform chemical transformations that remain synthetically challenging, and thus there is great interestin better understanding their active sites. The four-proton, four-electron reduction of dioxygen to water is one such transformation that is of interest because it provides a way to release energy stored in chemical bonds, with water as the sole byproduct.[7] Current technologies that efficiently perform this reaction use platinum[8] or palladium[9] electrodes which are prohibitively expensive. Instead, researchers are turning to nature for inspiration. Many enzymes involved in binding or activating oxygen (i.e., hemocyanin, tyrosinase, laccase, ascorbate oxidase, cytochrome c oxidase, etc.) have multiple copper atoms in their active sites. Biological[2,10] and synthetic (model)[11-18] multicopper systems are being intensely studied in order to better understand the fundamental ways

in which factors such as ligand environment, metal geometry, and proximity of additional metals modulate the structure of the multicopper core and tune oxygen reactivity.

One of the first synthetic complexes to demonstrate oxygen activation was a copper(I) complex supported by a tetradentate, tripodal amine-based ligand.[11,12] In the presence of oxygen, formation of a μ-1,2-peroxo dicopper(II) complex was observed, a reaction that is reversible if oxygen is removed with reduced pressure and heating. This model complex mimics reversible oxygen binding that occurs in hemocyanin. Several years later, the Tolman group reported that a tridentate amine copper(I) complex could reduce oxygen to give either a (μ-η^2:η^2-O_2) core (**A** in Figure 1.1) or a $(\mu\text{-}O)_2$ core (**B**), in which the oxygen double bond has been broken.[13] This represents a significant achievement because it has been proposed that oxygen activation at a dicopper site involves a similar intermediate.[14]

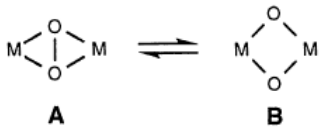


Figure 1.1. Interconversion of (μ-η^2:η^2-O_2) (**A**) and $(\mu\text{-}O)_2$ (**B**) cores is thought to occur during oxygen activation. In this case, M=Cu. Figure from Tolman, et al.[13]

The two examples given above involve dimerization of monocopper(I) complexes upon reaction with oxygen. Kinetically, this is not ideal because it requires the two copper(I) complexes to find each other in solution and attain the correct orientation with respect to the oxygen molecule. Additionally, if turnover of the reduced oxygen species to water is desired, the dicopper core must disassemble, resulting in a great deal of rearrangement and hence a large energetic barrier to catalysis. To address this issue, several groups have designed ligands that support two copper centers in close proximity.[15,16] These systems show interesting oxygen reactivity, and a variety of previously documented oxygen binding modes (see Figure 1.2) have been observed.

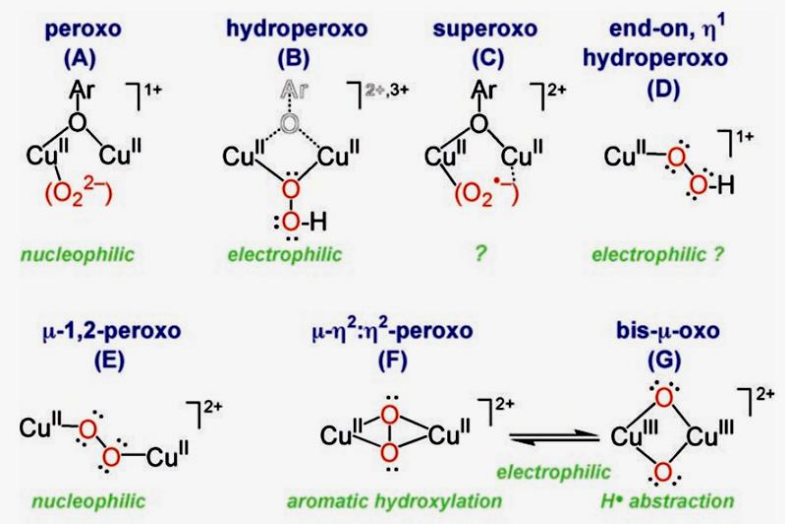


Figure 1.2. Binding modes of O_2 at dicopper sites. Figure from Hatcher and Karlin.[17]

The copper coordination of phenol-bearing ligands (XylO- and XylOH) has been studied for many years and has given rise to interesting multinuclear complexes in which the phenol oxygen bridges between adjacent coppers.[18] Separately, di(2-pyridyl) ketone (DPK) and its derivatives (acetal, hemi-acetal, or alkoxide) have been popular ligands for copper chemistry.[19] These ligands may coordinate to one copper either exclusively through the nitrogens,[20] through one nitrogen and the ketone oxygen,[21] or through both nitrogens and the alcohol oxygen.[22] In addition, multicopper structures have been reported with the alkoxide versions of DPK, in which the oxygen bridges to two coppers. Many of these structures feature a dicopper core[23], but tricopper[24], tetracopper[25], and higher nuclearity[26] alkoxide cores have also been documented. DPK-based ligands therefore exhibit a large range of possible coordination modes to copper, and hence seem appropriate for the study of multicopper assemblies.

Ligand Design and Synthesis

In a biological context, copper atoms are commonly coordinated by histidine nitrogens (as well as occasionally by oxygen- and sulfur-containing ligands).[27] The majority of biomimetic multicopper complexes reflect this trend, with nitrogen donors being the most prevalent type of ligand.[28] Hydrogen bonds and proton relays are present near the dicopper active sites in oxygen reducing proteins, and it is thought that they play a direct role in the mechanism of oxygen reduction to water.[29] Several reports have explored the use of proton relay ligands in oxygen reduction chemistry, but to date no such ligands have been used specifically with for copper chemistry.[30,31]

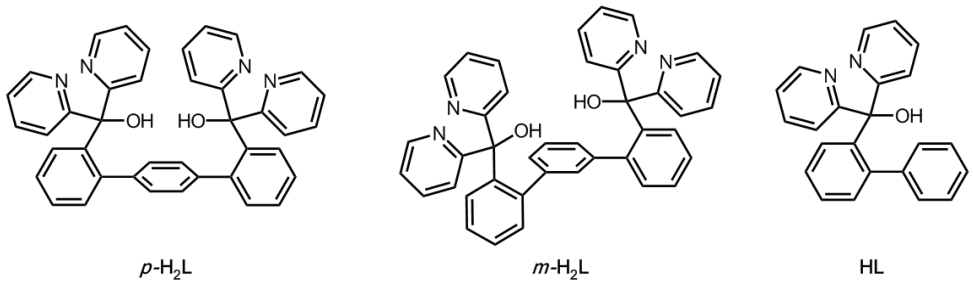
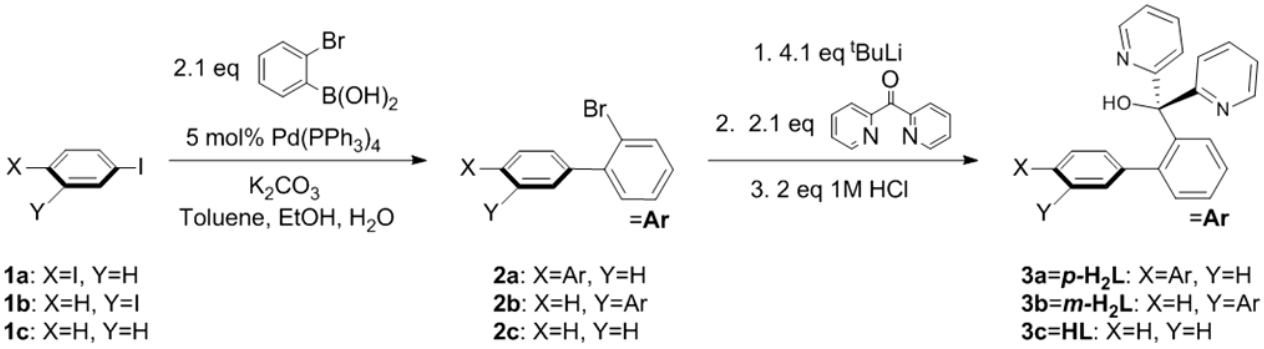


Figure 1.3. Three dipyridyl carbinol ligands with varying substitutions about the central aryl ring.

In this study, a series of three bidentate- and tetradentate ligands was designed to accommodate binding of multiple copper centers in rigid steric environments (Figure 1.3**)**. They possess an organic backbone for structural rigidity, pyridyl donors to coordinate copper, and hydroxyl groups that may serve either as proton relays or as additional ligands during the reduction of dioxygen to water. Varying the substitution about the central aryl ring imparts a different steric environment at the copper center and allows us to explore the relationship between ligand configuration and reactivity of the complexes. Notably, the distance between two coordinated coppers is expected to influence the geometry of any oxygen intermediates, as well as potentially of the resulting complexes.

Synthesis of the aforementioned ligands was accomplished in two steps. Starting from the appropriate diiodobenzene (**1a-c**), a Suzuki cross coupling reaction afforded dibromide (**2a-c**) (Scheme 1.1). Subsequent lithium-halogen exchange and treatment with 2,2'-dipyridylketone gave the desired ligands ***p*-H_2L**, ***m*-H_2L**, and **HL**. The modular synthetic approach easily accommodates possible modifications to the terphenyl- or biphenyl backbone or the pyridines.



1a: X=I, Y=H
1b: X=H, Y=I
1c: X=H, Y=H

2a: X=Ar, Y=H
2b: X=H, Y=Ar
2c: X=H, Y=H

3a=*p*-H_2L: X=Ar, Y=H
3b=*m*-H_2L: X=H, Y=Ar
3c=HL: X=H, Y=H

Scheme 1.1. Synthesis of dipyridyl carbinol ligands.

Coordination Chemistry with Cu(I)

Metallation of ***p*-H_2L** with one equivalent of copper(I) triflate toluene dimer immediately affords a bright yellow complex whose solid state structure is shown in Figure 1.4. The copper atoms are coordinated between two pyridyl groups and the alcohol moieties remain unbound. Two molecules of acetonitrile (solvent) complete the coordination sphere of each copper. Of note is the fact that the most stable configuration of this complex is that in which the coppers are coordinated on opposite faces of the central aryl ring. The anti configuration has the obvious disadvantage of holding the coppers too far apart for them to engage in cooperative reactivity with oxygen. However, one may expect that there is a relatively low barrier to rotation of one arm relative to the other in solution. Indeed, as evidenced by the broad nature of the pyridyl- and central aryl proton peaks, the two ligand arms appear to rotate freely on an NMR timescale (see

Appendix A). This indicates that both copper centers are transiently located on the same face of the terphenyl backbone, and hence that cooperative binding of small molecule substrates is feasible.

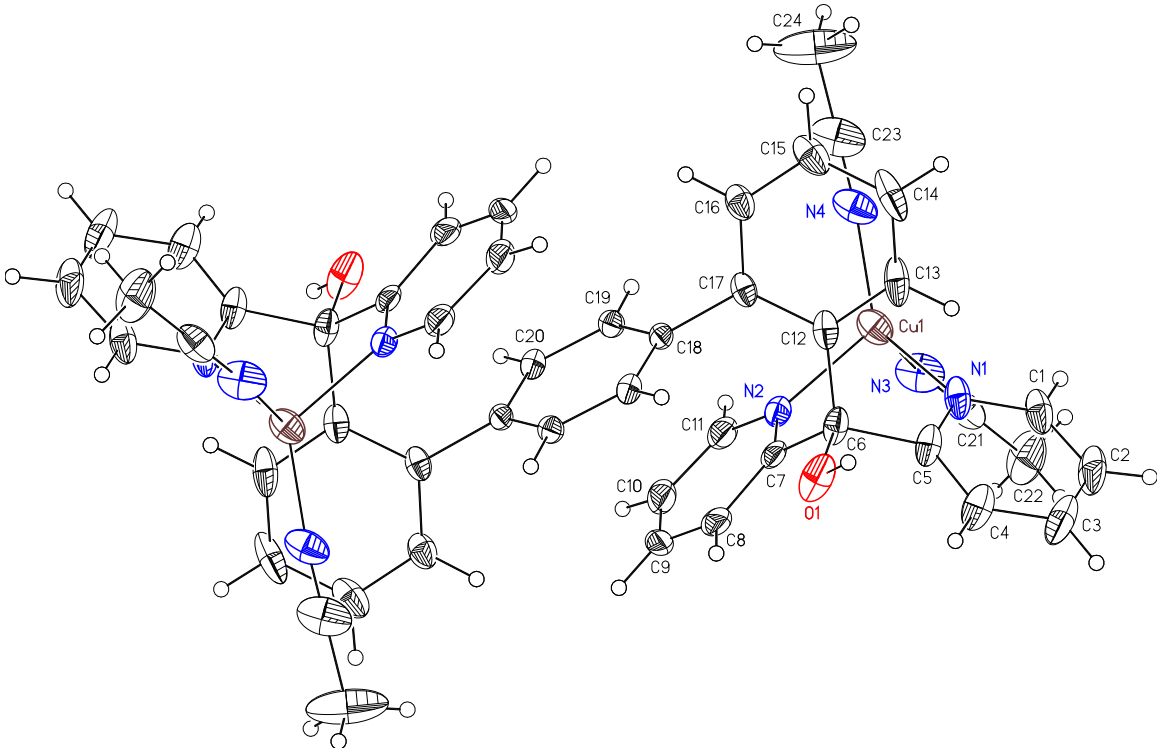


Figure 1.4. Solid state structure of [***p*-H_2LCu(I)$_2$(CH_3CN)$_4$](2OTf$^-$)** shown as 50% thermal ellipsoids. A tetrahedral Cu(I) atom is coordinated by each dipyridyl unit and two acetonitrile molecules. Metals are situated on opposite sides of the terphenyl backbone. Outer-sphere solvent molecules and counterions have been omitted.[32]

Reactions of ***m*-H_2L** and **HL** with the same Cu(I) source also led to bright yellow complexes which are believed to be structurally analogous, though we were unable to obtain solid state structures. On the basis of comparison of ^{1}H-NMR spectra, we conclude that Cu(I) coordinates with ***m*-H_2L** and **HL** in much the same way as with ***p*-H_2L**.

Coordination Chemistry with Cu(II)

Upon addition of two equivalents of copper(II) triflate to ***p*-H_2L** or ***m*-H_2L** (one equivalent for **HL**), dark blue NMR-silent complexes are formed. Characterization was accomplished via single crystal X-ray diffraction (XRD) (for the ***m*-H_2L** and **HL** variants only) and UV-visible absorption spectroscopy. The coordination mode of copper for ***p*-H_2L** is expected to be similar based on similarity of the ligand. Structures of **[*m*-H_2LCu(II)$_2$(CH$_3$CN)$_4$](4OTf)** (Figure 1.5) and **[HLCu(II)(CH$_3$CN)$_2$](2OTf)** (Figure 1.6) are shown below. As seen with the Cu(I) complexes, the coppers are located on opposite faces of the terphenyl plane, facing away from the central aryl. Each copper coordinates two pyridines, two acetonitrile molecules, and a triflate in a roughly square-pyramidal geometry. The alcohols once again remain unbound.

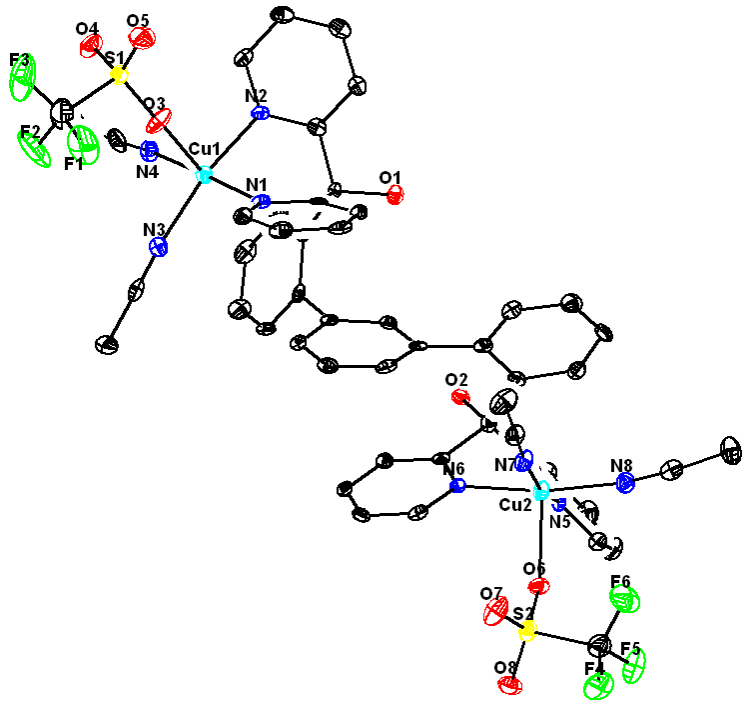


Figure 1.5. Solid state structure of **[*m*-H_2LCu(II)$_2$(CH$_3$CN)$_4$](4OTf$^-$)** shown as 50% thermal ellipsoids. A square- pyramidal Cu(II) atom is coordinated by each dipyridyl unit, two acetonitrile solvent molecules, and one triflate. Metals are situated on opposite sides of the terphenyl backbone. Hydrogens, solvent molecules, and outer-sphere counterions have been omitted.

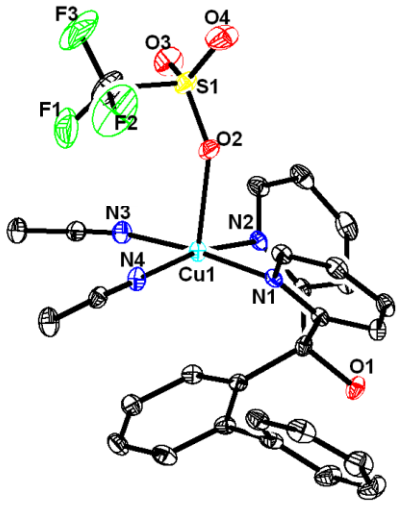


Figure 1.6. Solid state structure of [**HLCu(II)(CH$_3$CN)$_2$](2OTf$^-$)** shown as 50% thermal ellipsoids. A square-pyramidal Cu(II) atom is coordinated by the dipyridyl unit, two acetonitrile solvent molecules, and a triflate. Hydrogens and an outer-sphere counterion have been omitted for clarity.

Oxygen Reactivity: Formation of Copper Alkoxide Cores

Within several minutes of exposing **[*p*-H$_2$LCu(I)$_2$(CH$_3$CN)$_4$](2OTf$^-$)** (solution in CD_3CN) to 1 atm oxygen (excess), the solution turns green and a paramagnetic species is formed (reaction takes approximately 5 days to go to completion at room temperature). The crystal structure of the resulting complex, **[*p*-LCu(II)$_2$(CH$_3$CN)$_2$]$_2$(4OTf$^-$)**, reveals a D_2-symmetric dimer with two alkoxo-bridged dicopper(II) cores (Figure 1.7). In addition to the alkoxides, two pyridines (one from each ligand) and an additional acetonitrile molecule are coordinated to each copper, resulting in a distorted square pyramidal geometry. The structure reveals that the copper-oxygen core is slightly puckered—the second oxygen is 162° degrees out of the Cu-O-Cu plane. The copper core is a parallelogram with two sets of copper-oxygen bond lengths: 1.921 Å and 1.970 Å. The Cu-Cu distance is 2.885 Å and the O-Cu-O angle is 80.13°. Copper alkoxide cores are common in the literature[33]; an example of a copper alkoxide complex made using

hydrolyzed di-2-pyridyl ketone and pyridine has been shown to form a similar Cu_2O_2 bent parallelogram structure.[34] The authors report that the Cu-Cu distance is slightly longer (2.2837 Å), and the Cu-O distances are between 2.002 Å and 2.034 Å. Their dimeric hydrolyzed dipyridyl copper complex is stabilized by pyridine-pyridine π-π stacking interactions with a pyridine interplanar distance of 3.40Å. In our dimeric complex **[*p*-LCu(II)$_2$(CH$_3$CN)$_2$]$_2$(4OTf$^-$)**, two sets of pyridines are also observed to stack in this fashion with interplanar distances between 3.4 and 3.9 Å.

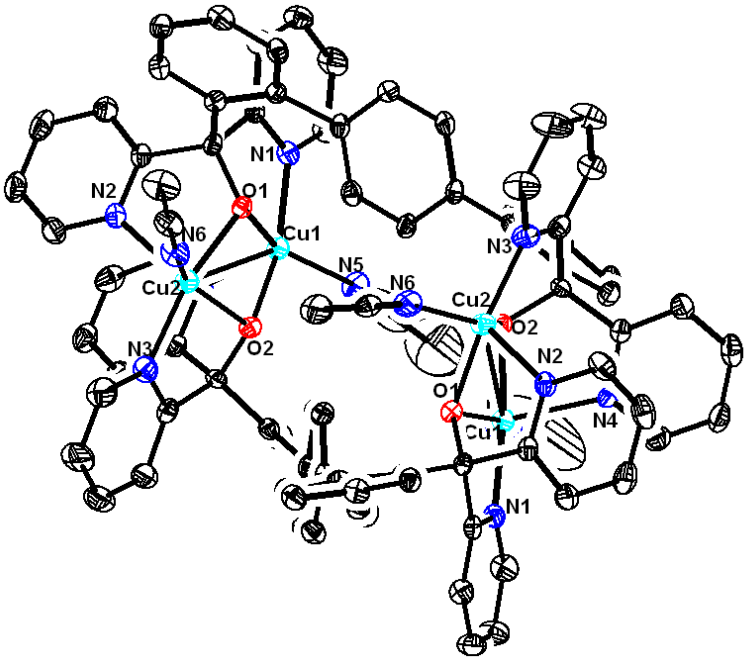
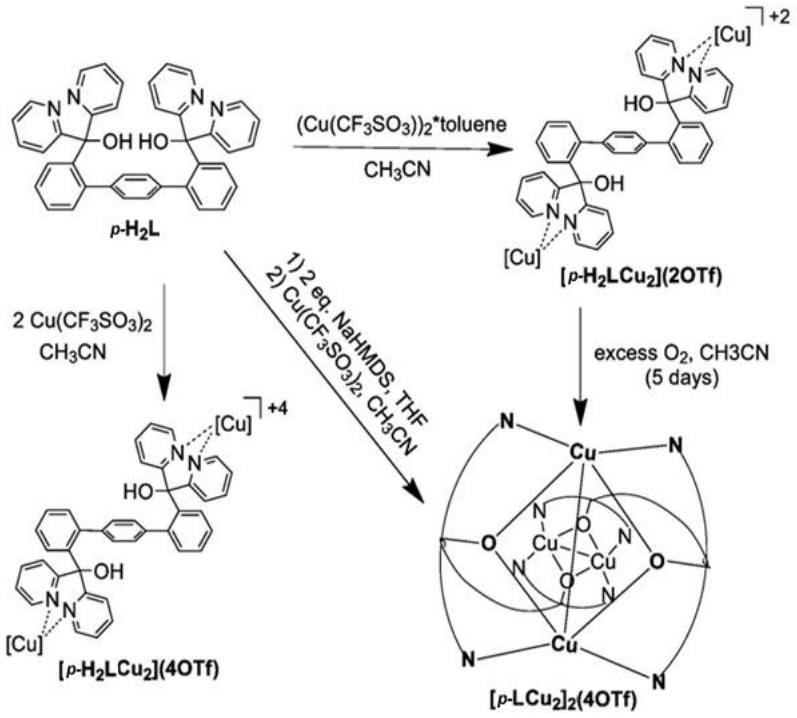


Figure 1.7. Solid-state structure of **[*p*-LCu(II)$_2$(CH$_3$CN)$_2$]$_2$(4OTf$^-$)** shown as 50% thermal ellipsoids. Each Cu(II) is coordinated by two pyridyls and two alkoxides (coming from different ligands), as well as one acetonitrile solvent molecule. Hydrogen atoms, outer-sphere solvent molecules and counterions omitted for clarity.

It is worth clarifying that the oxygen present in these structures is from the ligand alcohol group, not the O_2. It appears that the dioxygen is reduced to a highly basic intermediate which deprotonates the ligand hydroxyls and releases hydrogen peroxide. Similar reactions were performed with a 3-armed variant of the ligands presented here, but a peroxotitanyl test did not

indicate the presence of peroxide.[35] It may be that hydrogen peroxide is transiently formed, but goes on to react quickly with another equivalent of dicopper(I) complex. Preliminary support for this hypothesis is given by the observation that reaction of the dicopper(I) complex with excess H_2O_2 immediately yields the copper(II) alkoxide dimer, as evidenced by an identical ^{1}H-NMR spectrum. Scheme 1.2 summarizes the various metallation reactions of the ***p*-H_2L** ligand**.**



Scheme 1.2. Summary of metallation reactions with ligand ***p*-H_2L**.

Ligand ***m*-H$_2$L** shows a similar relationship; reaction of the Cu(I) complex with dioxygen or hydrogen peroxide leads to a vibrant green complex that can be independently synthesized upon reaction of the deprotonated ligand with Cu(OTf)$_2$. Though disordered, a solid state structure of the product reveals the formation of a similar Cu(II) alkoxide core, albeit with unexpected geometry (Figure 1.8). Instead of the previously observed dimeric Cu_2O_2 diamond-shaped core, this structure displays a trimer with two Cu_3O_3 cores that appear to be capped by triflates. The copper-alkoxide cores adopt a chair cyclohexane-like conformation in which each roughly square pyramidal copper coordinates a total of two pyridines and two alkoxides.

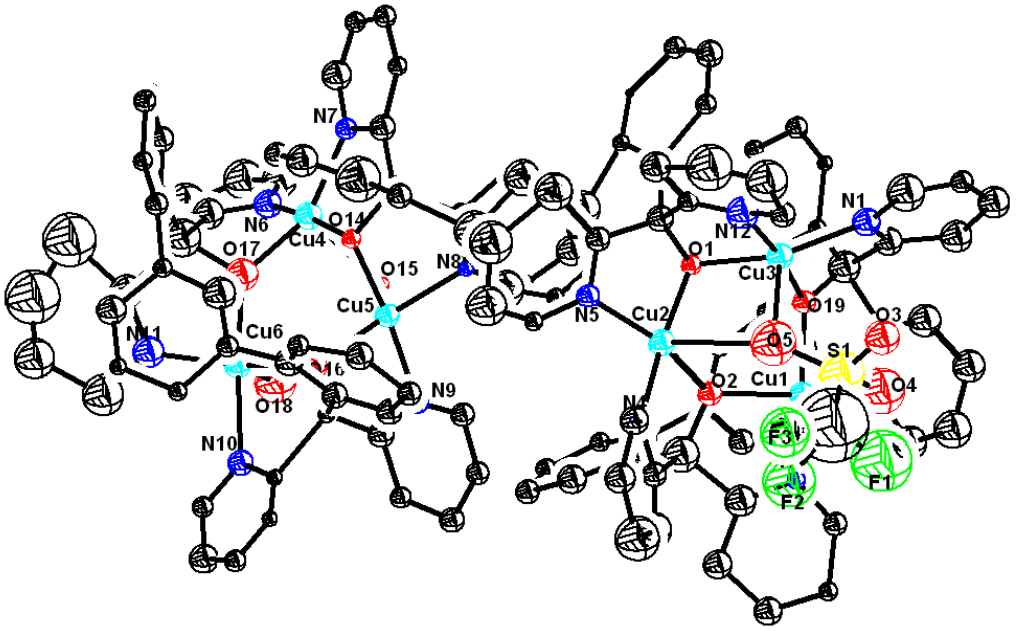


Figure 1.8. Solid-state structure of **[*m*-LCu(II)$_2$]$_3$(6OTf$^-$)** showing the Cu_3O_3 core (Cu1-O2-Cu2-O1-Cu3-O19) shown as a ball-and-stick model. Each Cu(II) is coordinated by two pyridyls and two alkoxides (coming from different ligands), and a triflate counterion caps the "chairlike" core through two oxygens. No acetonitrile molecules are coordinated. Hydrogen atoms and outer sphere counterions have been omitted for clarity. Structure has not been fully refined.

Perhaps unsurprisingly, reaction of the Cu(I) complex of **HL** with oxygen or hydrogen peroxide also results in the same complex as by ligand deprotonation and metallation with Cu(OTf)$_2$. For ligands ***p*-H$_2$L** and ***m*-H$_2$L**, the same copper alkoxide structures are always

formed, regardless of the specific reaction conditions (temperature, concentration, etc.). This is not the case for the **HL** derivatives. Two separate copper alkoxide products were isolated : a vibrant green dimer, **[LCu(II)(CH$_3$CN)]$_2$(2OTf)**, and a teal-blue trimer, **[LCu(II)(CH$_3$CN)]$_3$(3OTf)** (Figure 1.9). The **HL** ligand is therefore unique in that it accommodates the self-assembly of either the four- or six-membered cores, presumably because of reduced steric constraints compared to the two-armed analogs. Scheme 1.3 summarizes the various metallation reactions of the **HL** ligand**.**

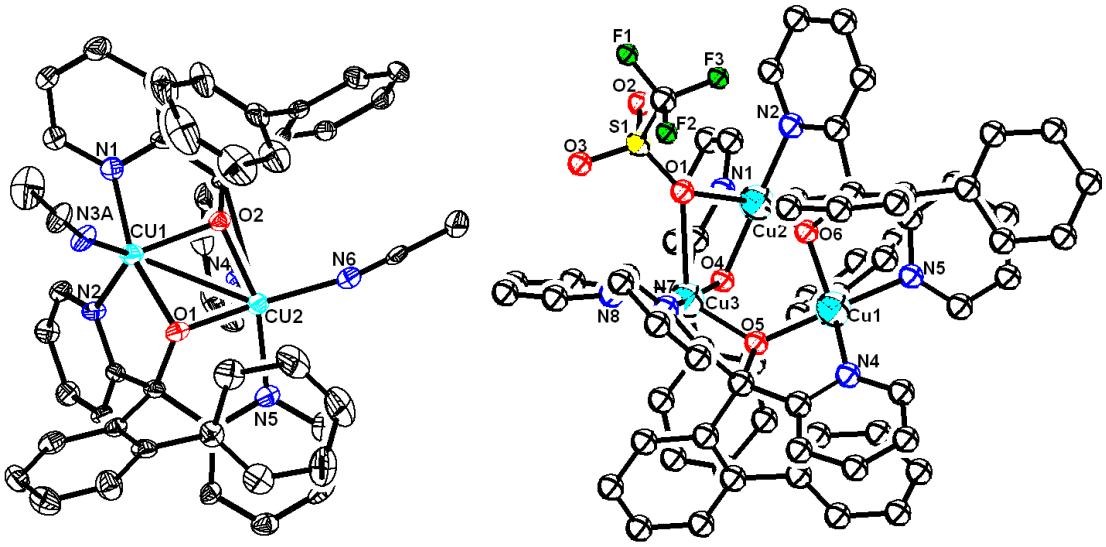
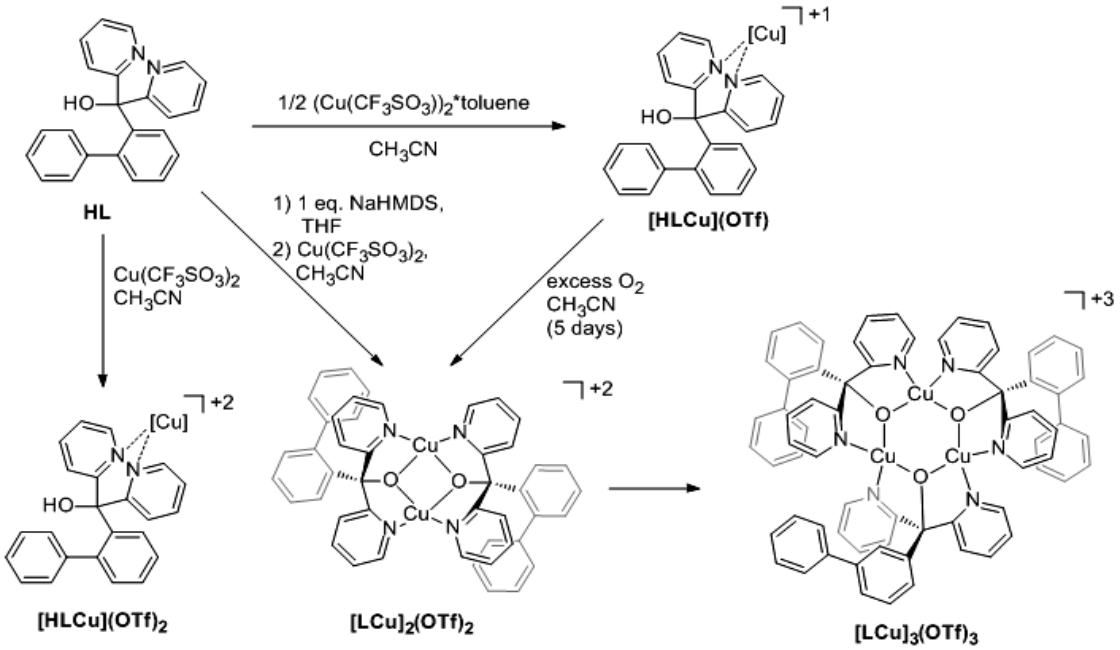


Figure 1.9. Solid state structures of **[LCu(II)(CH$_3$CN)]$_2$(2OTf)** (left) and **[LCu(II)]$_3$(3OTf)** (right). The left structure is shown as 50% thermal ellipsoids. Each Cu(II) is coordinated by two pyridyls and two alkoxides (from different ligands), as well as one acetonitrile solvent molecule. The right structure is shown as a ball-and-stick model. Each Cu(II) is coordinated by two pyridyls and two alkoxides (from different ligands), as well as one capping triflate counterion that is bound through one oxygen. Hydrogen atoms, outer-sphere solvent molecules and counterions omitted for clarity.

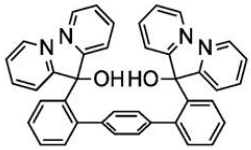
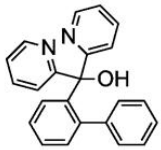
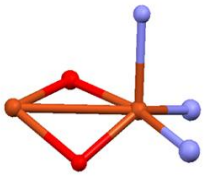
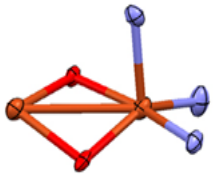
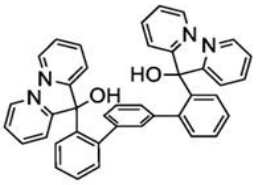
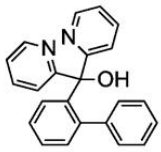
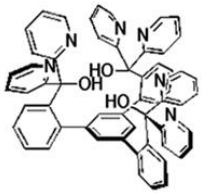
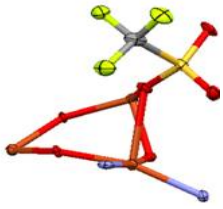


Scheme 1.2. Summary of metallation reactions with ligand **HL**.

Structural Comparisons Across Ligands

Table 1.1 summarizes the various copper alkoxide core structures formed with ligands ***p*-H_2L**, ***m*-H_2L**, and **HL**. Average Cu-Cu distances, Cu-O bond lengths, and O-Cu-O angles are included. 1,3-substitution about the central aryl ring appears to favor the formation of six-membered Cu-O cores, while 1,4-substitution shows a preference for four-membered cores. This is likely due to the fact that the copper binding sites of the para ligand are ideally placed to form an "X"-shaped dimer, while a trimer is formed with the meta ligand on account of its reduced bite angle. The reaction stoichiometry (one copper per alkoxide) therefore dictates that dimeric complexes feature Cu_2O_2 cores and trimeric complexes feature Cu_3O_3 sites. Because **HL** has comparatively little steric bulk, accommodates formation of both types of structure. All three structures are stabilized by π-stacking interactions, either between pyridine rings on different ligands, or between a pyridine and the central aryl ring on the same ligand.

A capping triflate counterion is coordinated in each of the six-membered Cu-O core structures. The triflate is coordinated through one (**HL**), two (***m*-H$_2$L**), or three (**H$_3$L'**) oxygens. This trend appears correlated with the O-Cu-O angle of 91.59°, 95.23°, and 96.46° respectively. As the Cu_3O_3 "chair" opens up (increasing O-Cu-O angle), the triflate anion is better able to coordinate to all three metal sites.

Cu_2O_2 Cores			
Ligand			
Complex	**[*p*-LCu(II)$_2$(CH$_3$CN)$_2$]$_2^{4+}$**	**[LCu(II)(CH$_3$CN)]$_2^{2+}$**	
Cu-O Core Structure			
Cu-Cu Distance	2.88 Å	2.88 Å	
Cu-O Bond Length	1.96 Å	1.96 Å	
O-Cu-O Angle	80.69 °	83.53 °	
Cu_3O_3 Cores			
Ligand			
Complex	**[*m*-LCu(II)$_2$(CH$_3$CN)$_2$]$_2^{4+}$**	**[LCu(II)(CH$_3$CN)]$_3^{3+}$**	**[L'Cu(II)$_3$]$^{3+}$ ***
Cu-O Core Structure			
Cu-Cu Distance	3.01-3.62 Å	3.09-3.60 Å	3.44-3.46 Å
Cu-O Bond Length	1.93-1.99 Å	1.90-1.95 Å	1.91-1.96 Å
O-Cu-O Angle	95.23 °	91.59 °	96.46 °

*Data from Tsui, et al.[35]

Table 1.1. Summary of Cu_2O_2 and Cu_3O_3 core structures obtained by reaction of Cu(I) complexes with oxygen. Key: Orange: Cu; Red: O; Blue: N; Gray: C; Green: F; Yellow: S

Spectroscopic Studies of the Cu_2O_2 and Cu_3O_3 Cores

Unlike the NMR-silent Cu(II) complexes, the dimeric and trimeric copper alkoxides exhibit broad yet well-defined paramagnetic peaks between 0 and 160 ppm. This indicates that the Cu-O cores have low-lying excited states.[36] The spectrum of **[*p*-LCu(II)$_2$(CH$_3$CN)$_2$]$_2$(4OTf)** is challenging to interpret due to the presence of ten peaks (Figure 1.10). Nine peaks would be predicted if all pyridines are related by symmetry, while thirteen peaks are expected if two pyridines are different. Peak integrals, T1 relaxation times[37], and gCOSY (see Appendix A) have so far not assisted in peak assignment of this complex.

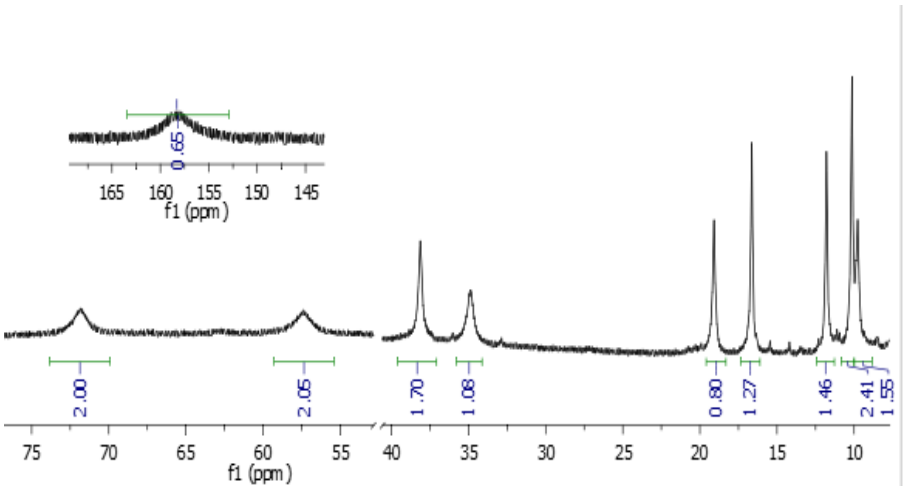


Figure 1.10. ^{1}H-NMR of **[*p*-LCu(II)$_2$(CH$_3$CN)$_2$]$_2$(4OTf)** (600 MHz, CD$_3$CN, 25°). Solvent peaks have been omitted.

The ^{1}H-NMR spectrum of **[LCu(II)(CH$_3$CN)]$_2$(2OTf)** in CD$_3$CN (Figure 1.11) shows seventeen peaks between 170 and 0 ppm. This spectrum indicates that at 25°C, the pyridine arms experience different chemical environments and are therefore distinct by NMR. Variable temperature (VT) NMR from -25 - 65°C shows coalescence of the seventeen peaks to only thirteen, demonstrating that exchange of the two pyridine orientations is no longer detected on an NMR timescale at temperatures above 55°C.

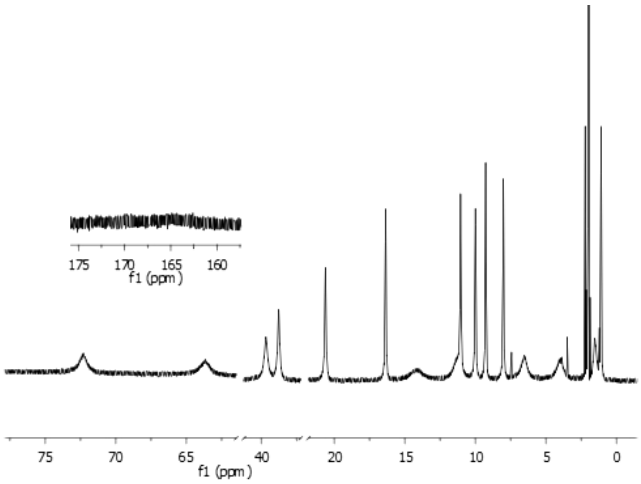


Figure 1.11. ^{1}H-NMR of **[LCu(II)(CH$_3$CN)]$_2$(2OTf$^-$)** (600 MHz, CD$_3$CN, 25°).

Electron Paramagnetic Resonance (EPR) studies of three copper alkoxide complexes show that the two complexes containing a Cu_2O_2 core display hyperfine splitting characteristic of Cu(II) complexes, while the Cu_3O_3-core containing complex has a broad spectrum with no hyperfine splitting visible. The simulation values of $g_{x,y}$, g_z, $A_{x,y}$, and A_z are given in Table 1.2. The EPR spectra presented here are typical for copper coordination compounds

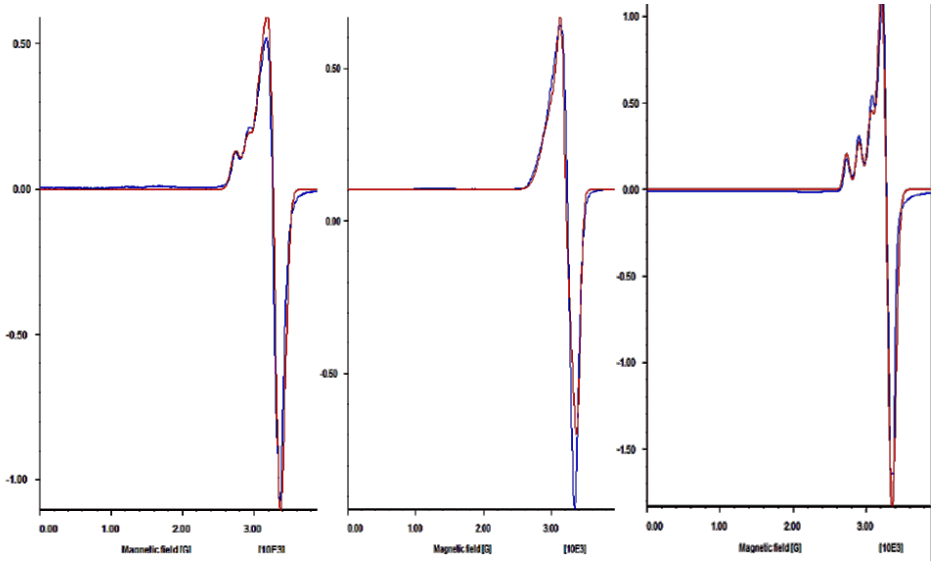


Figure 1.12. Experimental (blue) and simulated (red) EPR spectra at 10K of **[*p*-LCu$_2$]$_2$(4OTf$^-$)** (left), **[*m*-LCu$_2$]$_3$(6OTf$^-$)** (middle), and **[LCu]$_2$(2OTf$^-$)** (right).

Complex	$g_{x,y}$	g_z	$A_{x,y}$	A_z
[*p*-LCu_2]$_2$(4OTf)	2.031	2.235	104.570	490.000
[*m*-LCu_2]$_3$(6OTf)	2.043	2.250	160.740	132.000
[LCu]$_2$(2OTf)	2.028	2.245	50.570	480.000

Table 1.2. EPR simulation data for three copper alkoxide complexes

Conclusions

In summary, three similar ligands containing rigid organic frameworks, pyridine sites for copper coordination, and hydroxyl groups were synthesized and metallated with triflate salts of Cu(I) and Cu(II). Reaction of oxygen with Cu(I) complexes results in deprotonation of the hydroxyl groups and subsequent formation of di-, tetra-, and hexa-copper(II) cores with bridging alkoxos. The ^{1}H-NMR of these spectra have been studied, but peak assignments are complicated due to paramagnetism. EPR data of complexes containing Cu_2O_2 and Cu_3O_3 cores show that the former display hyperfine splitting while the latter give a broad spectrum.

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C h a p t e r 2

Toward CO_2 Reduction Chemistry with Terphenyl Diphosphine Rhenium Complexes

Introduction

As fossil fuel resources wane and atmospheric carbon dioxide concentrations continue to rise, alternative energy economies are receiving a great deal of attention. Carbon dioxide is released in large quantities during the combustion of carbon-based fuels, and its role as a greenhouse gas contributing to global climate change has been extensively documented.[1] In an effort to move to more sustainable and carbon-neutral fuel sources, it has been proposed to recycle CO_2 (either from industrial flue gas or simply from the atmosphere) and reduce it to methanol or other organic value-added products.[2,3,4] The benefits of such a process are evidently huge, but the difficulties are also imposing.

Thermodynamically, carbon dioxide is very stable and thus requires a large energy input to convert it to other products. Without efficient catalysts that are able to bind and activate CO_2, the amount of energy required to drive this process would remain prohibitive for industrial applications. Development of efficient carbon dioxide reduction catalysts necessitates an understanding of how slight modifications in steric or electronic properties affect reactivity and selectivity.

There are two main ways to approach the synthesis of liquid fuels from carbon dioxide: (1) complete reduction of CO_2 to a liquid fuel such as methanol, or (2) synthesis of a reduced intermediate such as CO, which can subsequently be converted into fuel.[5] The first method requires either one catalyst that can singlehandedly mediate multiple chemical transformations (*i.e.* CO_2 to CO to H_2CO to CH_3OH), or an ensemble of catalysts that work in concert. Both are currently lofty goals as they require the development of very sophisticated catalysts or a detailed understanding of how multiple catalysts function in concert. It is likely simpler to form CO, either by catalytic reduction of CO_2 or via the reverse water-gas shift reaction (eq 1).[6] Coupled with a renewable source of H_2, the CO may then be converted into hydrocarbons via the well-established Fischer-Tropsch process (eq 2).

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \text{(eq 1)}$$

$$(2n+1)\,H_2 + n\,CO \rightarrow C_nH_{(2n+2)} + n\,H_2O \qquad \text{(eq 2)}$$

The water-gas shift reaction is difficult to drive to completion and requires a large energy input, making it prohibitive for the synthesis of CO from CO_2. There is therefore a great interest in the development of a catalyst that would selectively reduce CO_2 to CO with water as the only byproduct. Due to the large reorganization energy required to pass from a linear molecule to a bent radical anion, the one-electron reduction of CO_2 to $CO_2^{\bullet -}$ is highly unfavorable (E°= -2.14 V vs SCE). It is more favorable to reduce carbon dioxide *via* proton-coupled multi-electron steps, resulting in production of water and CO, formic acid, formaldehyde, methanol or methane. Reduction potentials for these transformations are typically between – 0.45 V and – 0.85 V vs SCE.[7]

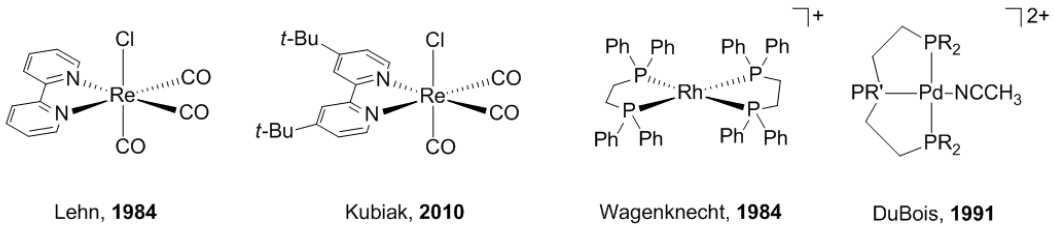


Figure 2.1. Selected second- and third-row transition metal complexes supported by bipyridyl- or phosphine ligands that catalyze CO_2 reduction.

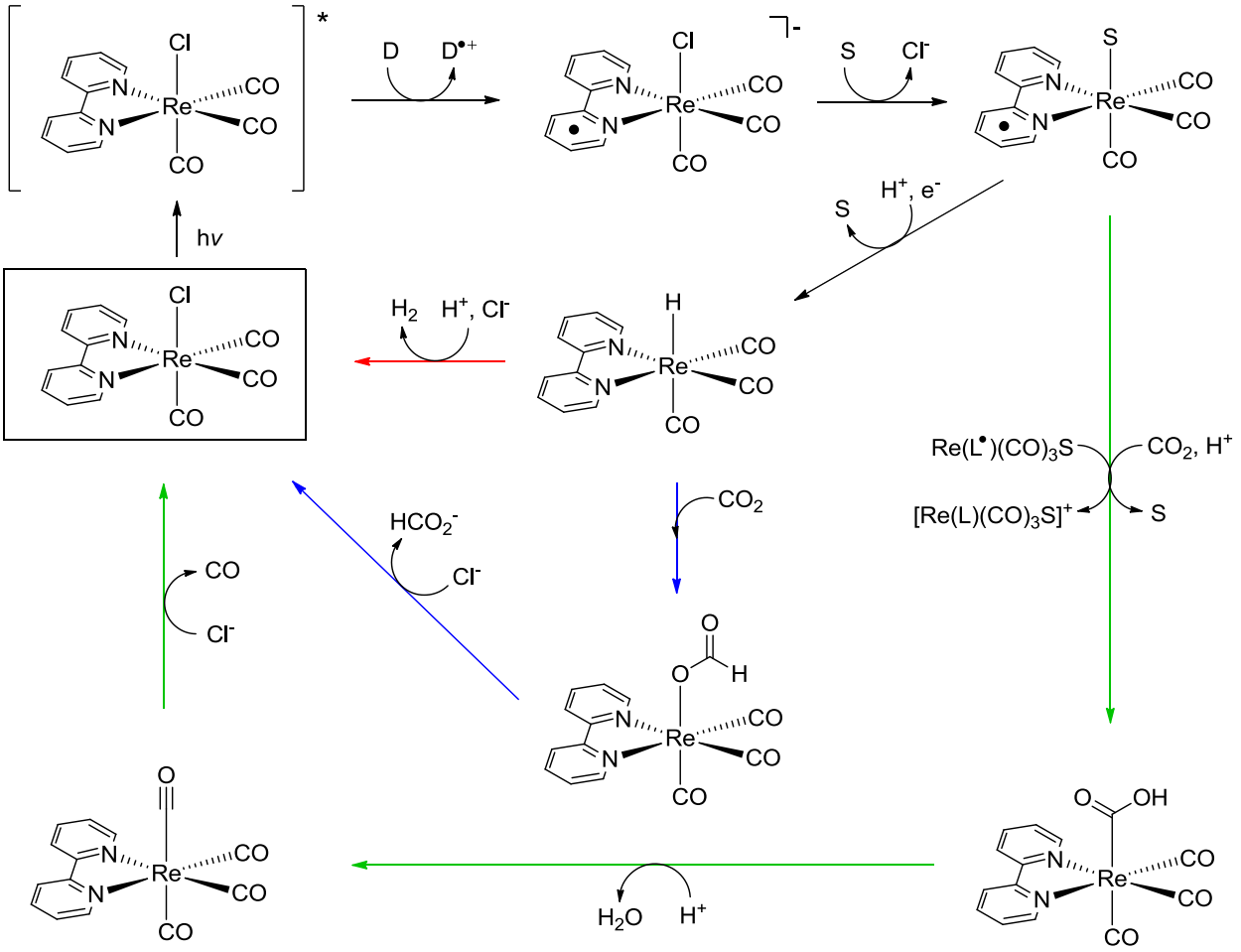
While there are many reports of various types of CO_2-reduction catalysts, we will focus here on homogeneous catalysts, specifically those supported by bipyridine- or phosphine ligands. These two motifs attracted our attention because they show promising reactivity with CO_2 and can be readily altered to tune steric and electronic environments about the metal.

Wagenknecht's $Rh(dppe)_2Cl$ (dppe = 1,2-bis(diphenylphosphino)ethane), the first reported transition metal-phosphine, converts CO_2 to formate (E = -1.55 V vs SCE) with short-term current efficiencies of 40%.[8] A series of triphosphine palladium complexes from the DuBois group exhibit high

catalytic rates (10-1000 M^{-1} s^{-1}), high selectivities for CO production (>90%), and low overpotentials (10-300 mV), but have low turnover numbers (typically 10-100).[9,10] The triphosphine ligands used could be easily modified to probe how steric and electronic effects dictate reactivity. DuBois and coworkers varied the central donating atom of their ligand (see Figure 2.1) and found that the highest catalytic activity occurred with the original triphosphine ligand, indicating that phosphines may be well suited to the electronic requirements for catalysis.[11]

A well-known example of a metal-bipyridine complex is the Lehn catalyst, $Re(bipy)(CO)_3Cl$. The Lehn catalyst is robust and has a high Faradaic efficiency (98%), but suffers from low rate constants and turnover numbers.[12,13] Selective reduction of CO_2 to CO occurs in a 9:1 DMF:H_2O solution, with no H_2 formation observed. As the concentration of water is increased, the reduction of H_2O to H_2 occurs as well. When no CO_2 is present, hydrogen gas is the sole reduction product. These findings indicate that the mechanism for CO versus H_2 production must compete with each other as the amount of water in the system increases. Additionally, use of different amine sacrificial donors alters the CO/H_2 ratio.

Proposed mechanisms for H_2 (red), HCO_2^- (blue), and CO (green) formation with Lehn's catalyst are shown in Scheme 2.1.[14] $Re(bipy)(CO)_3Cl$ (boxed) undergoes a metal-to-ligand charge transfer and is then reductively quenched by a donor (often an amine) to give a complex in which a radical anion is located on the ligand. Replacement of the chloride by a solvent molecule yields the catalytically active species. Experiments by Ishitani, et al. suggest that formation of a 2-electron reduced carbon dioxide adduct occurs via formation of a carboxylate-bridged dimer.[15] This proposal has been further explored using Density Functional Theory (DFT).[16] Acid-promoted hydrolysis gives a tetracarbonyl rhenium complex which subsequently loses one molecule of CO and re-coordinates a chloride. This last step is supported by labeling experiments that show full incorporation of $^{13}CO_2$ to form $Re(bipy)(^{13}CO)_3Cl$. Although certain aspects of the mechanism are still up for debate, it appears that the catalytic successes of the Lehn catalyst are due in part to the ligand's ability to act as an electron reservoir.[17] In this fashion, electrons may be formally localized on the ligand and then subsequently transferred to the metal and then the π^* orbital of CO_2.



Scheme 2.1. Proposed mechanisms for generation of H_2 (red), HCO_2^- (blue), and CO (green) using the Lehn catalyst. The starting complex is boxed. D is a sacrificial amine donor and S is a solvent molecule. Figure adapted from Morris, et al.[14]

In the years since Lehn's initial publication, other groups have studied 2,2'-bipyridyl-[18] and 4,4'-dimethyl-2,2'-bipyridyl[19,20] tricarbonyl rhenium(I) complexes in the context of CO_2 reduction activity. The Alberto group has investigated fluorescence properties and catalytic activity of rhenium(I) and technetium(I) diimine tricarbonyl complexes.[21] Most recently, the Kubiak group demonstrated that by changing the electron donating/withdrawing nature of the substituents at the 4,4'-position on the bipyridyl group, turnover number and frequency of the original catalyst could be improved. As expected, the first and second reduction potentials became increasingly more negative with more electron donating substituents, however catalytic ability followed a more complicated trend.[22] The complex with the most negative reduction

potential should have the most nucleophilic rhenium center and thus is expected to be the best CO_2 reduction catalyst. However, the methoxy substituted complex showed essentially no catalytic activity while the *tert*-butyl substituted complex exhibited excellent activity. The authors propose that this surprising result may be due to differences in π- and σ-donor strength of the substituents.

As evidenced by the above discussion, design of 2nd-row transition metal phosphine- or bipyridine-based CO_2 reduction catalysts requires a solid understanding of how the metal(s) and ligands synchronize to produce an environment that is favorable for catalysis. The Lehn catalyst and its analogues are promising because of their efficiency, robust nature, and ease of modular synthesis. Phosphine-based systems have demonstrated high rates of conversion and low overpotentials. We seek to develop a new family of rhenium(I) carbonyl phosphine complexes and study their structural and electrochemical properties. Our study will seek to better understand how a new phosphine ligand affects CO_2 reduction at a well-characterized rhenium(I) carbonyl center.

Ligand Design

We discuss progress towards the synthesis and characterization of a new family of rhenium-phosphine complexes which incorporate aspects of Lehn's system (a rhenium(I) carbonyl chloride) while using a bidentate phosphine ligand in place of bipyridine. The phosphine ligands used here have been previously explored in the Agapie group in the context of mono- and dinuclear nickel complexes.[23,24,25,26] Based on prior research, these ligands are expected to bind one rhenium between the two phosphine arms, with possible agostic interactions coming from the central aryl ring. Given the steric and electronic differences of these complexes compared to more traditional rhenium bipyridine, the new rhenium phosphine complexes may exhibit interesting reactivity and possibly the ability to catalytically reduce CO_2 to CO.

Two parent terphenyl diphosphine ligands, ***m*-P_2** and ***p*-P_2**, were synthesized according to previous procedure.[23,26] These ligands feature a rigid backbone with two phosphine "arms" situated at varying

positions about the central aryl ring. The phosphine arms are able to rotate at varying degrees with respect to the cental aryl, and thus can flexibly accommodate coordination of a metal.

Synthesis and Structure of Parent Re(I) Bisphosphine Complexes

Both ligands were metallated with a rhenium (I) carbonyl halide salt, $ReX(CO)_5$ (X = Cl or Br). This step requires forcing conditions to drive carbon monoxide dissociation. Initially, the reactions were run with $ReCl(CO)_5$ in toluene at 100 °C, but even after 36 hr the reaction was not complete and did not appear to be forming one species cleanly (as determined by ^{31}P-NMR spectroscopy). Metallation with $ReBr(CO)_5$ was also attempted in toluene at 100 °C, but even after 4 days of heating the desired product could not be isolated in good yield. Increasing the temperature to 130 °C (with *m*-xylene as solvent) and using $ReCl(CO)_5$ as a rhenium source allowed the desired rhenium phosphine complexes to be isolated in good yield (62% for meta complex, 64% for para complex). The ***m*-$\mathbf{P_2}$** ligand was substantially easier to metallate, requiring only 24 hr to go to completion compared to 6 days for the ***p*-$\mathbf{P_2}$** ligand. This is likely due to the fact that the reduced distance between phosphines in the ***m*-$\mathbf{P_2}$** ligand allows rhenium to coordinate more easily. Even in *p*-xylene at elevated temperatures, metalation with $ReBr(CO)_5$ did not proceed cleanly and appeared to be slower than metalation with the analogous chloride. For this reason, $ReCl(CO)_5$ was chosen as the rhenium source for the remainder of the project.

The ***m*-$\mathbf{P_2ReCl(CO)_2}$** and ***p*-$\mathbf{P_2ReCl(CO)_2}$** complexes were characterized by ^{1}H- and ^{31}P-NMR spectroscopy, IR spectroscopy, and X-ray diffraction. Both complexes show one peak by ^{31}P-NMR and two sets of methine peaks by ^{1}H-NMR, indicating that both are of C_s symmetry. Infrared (IR) spectroscopy (solution in CH_2Cl_2) shows two carbonyl stretching frequencies for both complexes.

A crystal structure of ***m*-$\mathbf{P_2ReCl(CO)_2}$** reveals a nearly square pyramidal rhenium coordinated between the two phosphine arms (Figure 2.2). The rhenium center is almost directly above the 2-position central aryl carbon and the chloride is bound on the side facing away from the central aryl ring. The average distance from the rhenium to the nearest central aryl carbon is 2.605 Å. This distance is long enough to

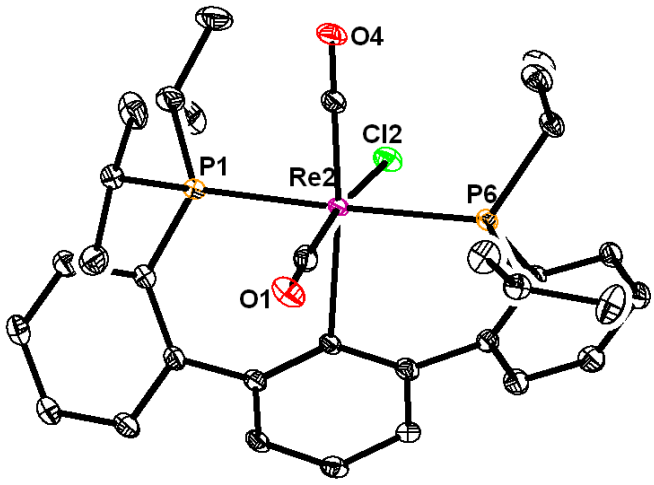


Figure 2.2. Solid-state structure of ***m*-$P_2ReCl(CO)_2$** shown as 50% thermal ellipsoids.

indicate some type of agostic interaction, though the exact nature of this interaction (with one aryl carbon) is not particularly clear. A solid-state structure was not obtained for ***p*-$P_2ReCl(CO)_2$**, but an analogous bromide complex made in the Agapie group has been structurally characterized.[27] The structure of ***p*-$P_2ReCl(CO)_2$** is expected to be similar, a hypothesis that is corroborated by ^{1}H-, ^{31}P-NMR, and IR spectra. The crystal structure of the bromide complex reveals an agostic interaction between the rhenium and the central aryl π-system (perpendicular Re-C distance is 2.360 Å) and the average Re-P bond length is 2.490 Å (Figure 2.3). The position of the rhenium center with respect to the central aryl ring differs between complexes, as well as the angle at which the phosphine arms are bent to accommodate the metal. In both structures, the halide is coordinated on the side opposite the central aryl, presumably due to electronic repulsion with the π-system.

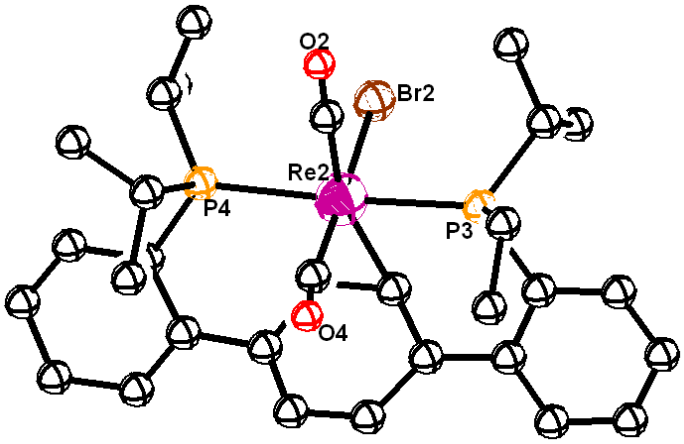


Figure 2.3. Solid-state structure of ***p*-P$_2$ReBr(CO)$_2$** shown as a ball-and-stick model.

Cyclic Voltammetry Studies

Cyclic voltammetry (CV) experiments were performed to study the electrochemical properties of these rhenium complexes and their potential to catalyze CO_2 reduction. Under N_2 atmosphere, the cyclic voltammograms of the meta and para complexes are similar and show three distinct oxidative waves and two reductive waves (Figure 2.4). One explanation for these redox features is that the neutral Re(I) phosphine undergoes a one-electron reduction (**a**) to form a radical anion, which exists in equilibrium with the chloride-dissociated complex. If the two Re(0) species exist in comparable quantities, two oxidation processes are possible (**b** and **c**): oxidation of the radical anion back to the starting species, or oxidation of the rhenium-based radical to a cationic complex followed by re-association of a chloride ion. We assign the quasireversible process **d**/**e** ($E_{1/2}^{ox}$ = 0.686 V for ***p*-P$_2$ReCl(CO)$_2$** and $E_{1/2}^{ox}$ = 0.747 V for ***m*-P$_2$ReCl(CO)$_2$** vs Ag/Ag$^+$) to the Re^I/Re^{II} couple. Literature values for the Re^I/Re^{II} potential are in the range of 0.80 V to 1.11 V vs Ag/Ag$^+$ for $[Re(dmb)(CO)_2(PR_3)(PR'_3)]^+$ complexes (dmb = 4,4'-dimethyl-2,2'-bipyridine),[28] 0.85 V to 1.57 V vs Ag/Ag$^+$ for $[Re(CO)_2(N\text{-}N)(P\text{-}P)]^+$ complexes (N-N = bidentate N-donor ligand and P-P is a bipyridine),[29] and 0.71 V to 1.27 V vs Ag/Ag$^+$ for $[Re(CO)_n(N\text{-}N)(PPh_3)_2Cl_{2-n}]$ (N-N = bidentate N-donor or two monodentate N-donors; n = 1,2).[30]

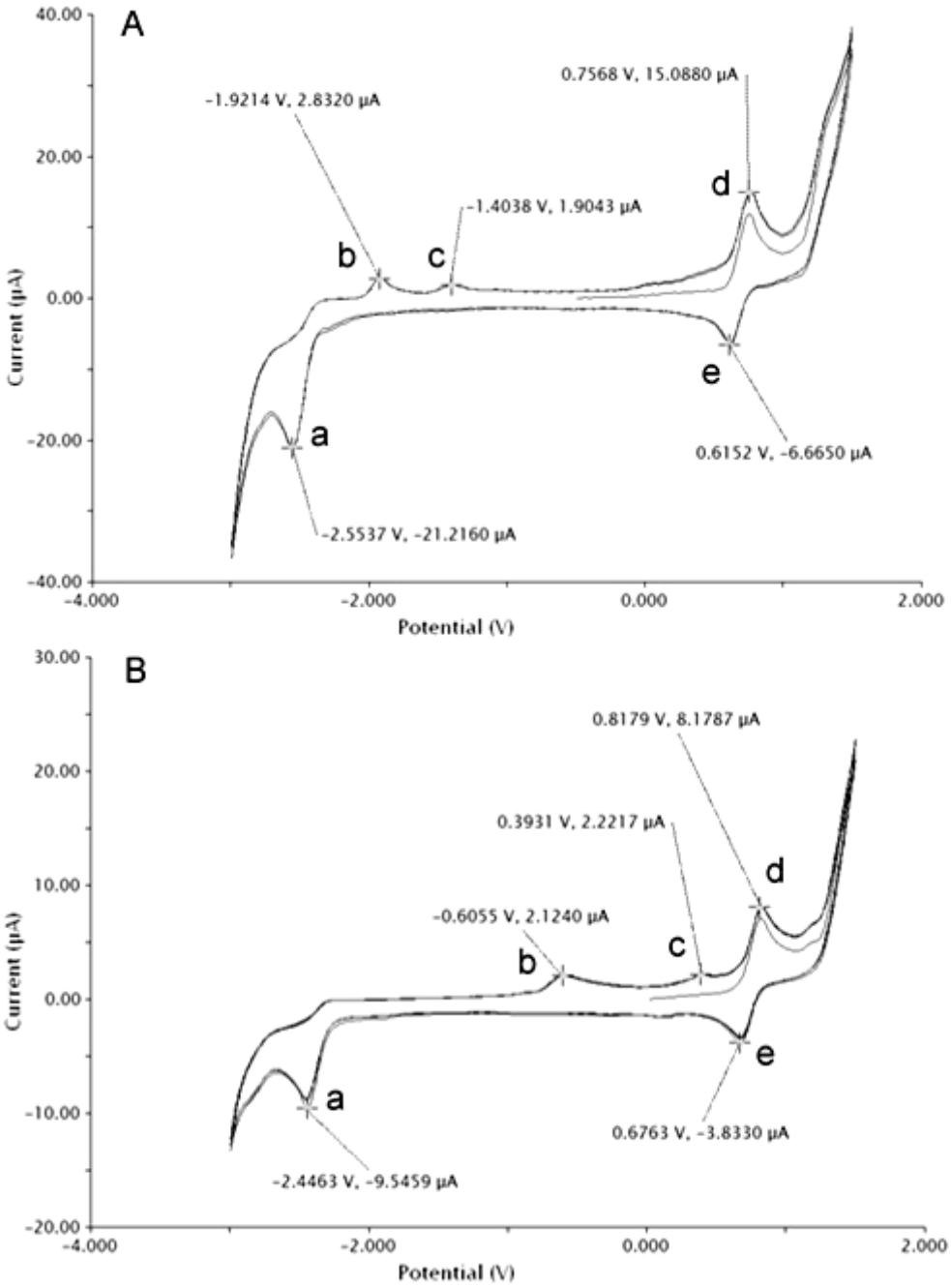


Figure 2.4. Cyclic voltammograms of A) ***p*-$P_2ReCl(CO)_2$** and B) ***m*-$P_2ReCl(CO)_2$**. Scans taken of 0.5 mM complex in THF with 0.1 M TBAP electrolyte using a glassy carbon electrode and Ag/Ag^+ reference electrode.

Several electrochemical observations support this proposal, though assignments are not unambiguous. When the potential is varied from -1.5 V to 1.5 V (i.e., not far enough to reduce the Re(I) complex to its radical anion), the oxidation waves assigned to processes **b** and **c** are not observed. Likewise, when the potential is not sufficiently positive to oxidize the Re(I) complex, only the peaks corresponding to processes **a**, **b**, and **c** are observed. A second observation is the decreased area of the **b** and **c** oxidation waves, relative to the others. Smaller integrals would be expected if the amount of material undergoing each oxidation was roughly half of that undergoing the other redox steps.

The roughly 60 mV difference in Re(I)/Re(II) oxidation potential reflects the extent of interaction between the rhenium and the central aryl; ***p*-$\mathbf{P_2ReCl(CO)_2}$** is more easily oxidized due to its agostic interaction with the ring. Similarly, the proposed Re(I)→Re(0) reduction occurs at a more negative potential for the ***p*-$\mathbf{P_2ReCl(CO)_2}$** complex and is reflective of the increased electron density at the metal center. Notably, the irreversible **b** and **c** oxidations vary widely between the *meta*- and *para*-complexes. Given the proposal above, the Re(0) oxidation potentials would be highly dependent on their stability and hence dependent on chloride dissociation. Both oxidation potentials are significantly lower for the para complex, indicating that the Re(0) radical anion and radical species are unstable. This contrasts with the meta complex, where oxidation occurs at relatively higher potentials. This may be explained by the fact that reduced Re-aryl distance in the para complex destabilizes reduced species.

Follow-up experiments to further substantiate the chloride dissociation proposal are needed. The peak ratio **b**/**c** is expected to exhibit scan rate dependence if the process involves one-way chloride dissociation from the reduced Re(0) species. Classical mercury-based polarography[31] offers a way to quantify free chloride concentration before and after reduction, and could therefore be used to clarify whether the dissociation is one-way or exists in equilibrium. Separate electrochemical studies of the cationic rhenium complex (no chloride) may be compared, with changes in the two voltammograms attributable to chloride-dependent processes.

Synthesis and Structure of Modified Re(I) Bisphosphine Complexes

As previously mentioned, multi-electron reductions of CO_2 are more favorable because they result in the formation of molecules that are more stable. In order for the catalyst to reduce carbon dioxide by more than one electron, it must be able to be reduced multiple times (Kubiak proposes that the active catalytic species is effectively a Re(-I) complex). Because ***m*-P_2ReCl(CO)$_2$** and ***p*-P_2ReCl(CO)$_2$** have very negative first reduction potentials, a second reduction is simply not feasible and these complexes are not expected to display catalytic activity. Cyclic voltammograms of both complexes were taken under 1 atm CO_2 atmosphere, and no substantial increase in current was observed.

A review of the literature shows that most CO_2-reduction catalysts have first reduction potentials between -1.0 V and -1.2 V vs. SHE.[5] Owing to the extreme reduction potentials of the two parent rhenium complexes (-2.75 V and -2.65 V vs. SHE for ***m*-P_2ReCl(CO)$_2$** and ***p*-P_2ReCl(CO)$_2$** respectively), we aspired to synthesize second generation ligands that would allow for more facile reduction. This may be accomplished either by employing an easily reduced ligand that will subsequently undergo charge transfer to the metal center, or by focusing on redox chemistry on the metal and employing ligands that will help stabilize a reduced (i.e., Re(0) or Re(-I)) metal center.

Two modified diphosphine ligands, ***m*-P_2(NMe$_2$)OMe** and ***m*-P_2(*t*-Bu)OMe**, retain the meta-terphenyl geometry of ***m*-P_2** but include additional substituents on the central aryl ring.[32] Metallations of both ligands were performed with $ReCl(CO)_5$ in xylene at 130°C, but unexpected differences in reactivity were observed. Metallation of the dimethylamino variant went to completion after 24 hr and yielded one major product, while the identical reaction using the *tert*-butyl variant led to a species showing two distinct phosphorus NMR peaks in a 1:1 ratio.

Characterization of the two products was done by ^{1}H- and ^{31}P-NMR spectroscopy and X-ray diffraction (for the $N(Me)_2$ variant). A solid state structure reveals that a rhenium(I) dicarbonyl chloride is coordinated between the two phosphine arms and has activated the O-CH_3 bond of the ligand with presumed loss of MeCl (Figure 2.5). Similar activation has been observed with Ni(II) complexes of this ligand,[33] and indicates that the original Re(I) center is significantly nucleophilic in character. Rhenium

coordination to the phenoxide causes noticeable distortion of the rhenium geometry away from octahedral (the average P-Re-P bond angle is 167.31°). Compared to the parent ***m*-P_2ReCl$(CO)_2$** complex (see Figure 2.2), the rhenium is shifted away from the central aryl ring, forcing the two phosphine arms to one side of the ligand plane. There are two molecules in the asymmetric unit, one with a trigonal pyramidal geometry on the dimethylamino nitrogen and one in which electron density is present in two locations (shown). We presume that this is due to disorder in the crystal structure, but it may also be an indication of the existence of resonance forms in which the nitrogen adopts a planar geometry. ^{31}P-NMR spectroscopy indicates one peak, and the -OCH_3 protons are no longer visible by ^{1}H-NMR.

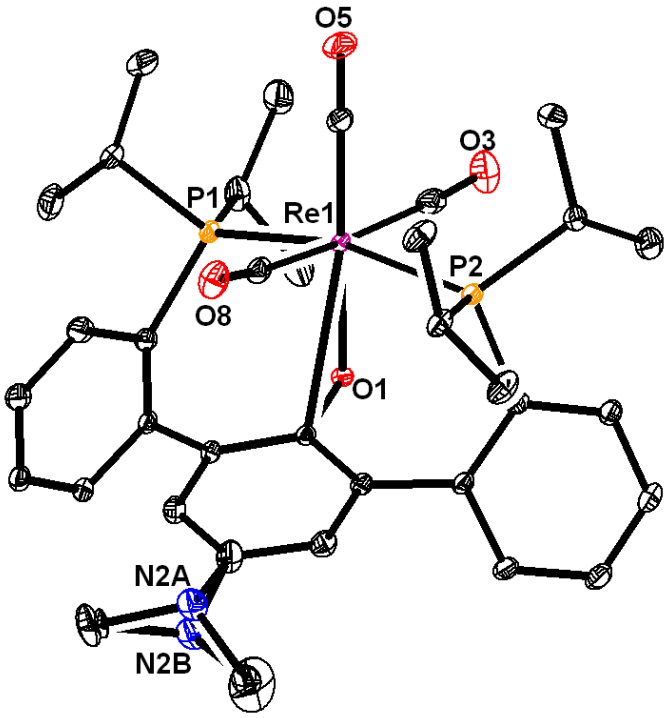


Figure 2.5. Solid state structure of **[(*m*-P_2(N$(Me)_2$)ORe$(CO)_3$)]** shown as 50% thermal ellipsoids.

Future Work

Future work in this area will focus on the synthesis of quinone variants of ***m*-$\mathbf{P_2}$** and ***p*-$\mathbf{P_2}$**, which are expected to display interesting electrochemical properties due to the non-innocence of the ligand. The quinone may function similarly to bipyridine (i.e., as an electron reservoir) and facilitate a ligand-to-metal charge transfer process. Additionally, one may imagine interesting coordination chemistry of the quinone-based ligands as a function of oxidation state and degree of protonation.

Conclusions

Metallation of a family of terphenyl diphosphine ligands with rhenium(I) carbonyl salts reveals that one rhenium atom is coordinated per ligand in a configuration that is dependent on the ligand geometry (*meta*- vs *para*-) and substitution (-H vs -OMe and *t*-Bu vs $N(Me)_2$). The rhenium complex with unsubstituted meta ligand shows no agostic interactions with the central aryl ring, while a close analog made with unsubstituted para ligand does interact with the ring π-system. Differences in reactivity with rhenium are observed: the $N(Me)_2$ variant yields one major product while the *t*-Bu variant does not metallate cleanly. Electrochemical studies of the unsubstituted rhenium complexes show that their reduction potentials are very negative and suggest that chloride may dissociate from rhenium when reduced. These results add to our understanding of redox chemistry at phosphine-supported rhenium centers, which has the potential to allow us to design more effective CO_2 reduction catalysts.

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A p p e n d i x A

Chapter 1 Supporting Information:
Synthesis, Structures, and Characterization of Multicopper Complexes
Supported by Dipyridylcarbinol Ligands

Experimental Details

General considerations. All air- and moisture-sensitive compounds were manipulated using standard Schlenk or Cannula techniques or in a glove box under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried using the method of Grubbs.[1] Acetonitrile-d_3 was purchased from Cambridge Isotopes and distilled from calcium hydride. Other materials were used as received. UV-Vis measurements were obtained on a Varian Cary 50 spectrophotometer using standard or anaerobic quartz crystal cells. ^{1}H-NMR spectra were recorded on Varian Mercury 300, Varian 400 MR, Varian INOVA-500, or Varian 600 MHz spectrometers, at room temperature unless indicated otherwise. Chemical shifts are reported with respect to internal solvent: 1.94 ppm (CD_3CN) for ^{1}H-NMR data. Gas chromatography-mass spectrometry (GC-MS) analysis was performed upon treating reaction mixtures with dichloromethane and filtering through a plug of silica gel. Elemental analyses were performed by Midwest Microlab, LLC, Indianapolis, IN.

Unless indicated otherwise, all commercial chemicals were used as received. Tert-butyllithium solution in THF and sodium bis(trimethylsilyl)amide were purchased from Alfa and Aldrich, respectively. Di(2-pyridyl)ketone was purchased from Aldrich or from Frontier Chemicals. Copper(II) triflate was purchased from Strem. Copper(I) triflate toluene dimer was prepared according to literature procedure.[2]

Synthesis of 1,4-bis(2-di(2'-pyridyl)hydroxymethylphenyl)benzene (*p*-H_2L): 1,4-bis(2-bromophenyl) benzene (prepared according to literature procedure[3]) (2.190 g, 5.64 mmol, 1 equiv) was dissolved in Et_2O and frozen in a coldwell. 15.07 mL (23.14 mmol, 4.1 equiv) of 1.53 M ^{t}BuLi (solution in THF) were added dropwise to the thawing solution and allowed to react for 1 hr at ambient temperature. A solution of di(2-pyridyl) ketone (2.182 g, 11.85 mmol, 2.1 equiv) in Et_2O was added dropwise. The reaction was allowed to run overnight and was subsequently quenched with 11.28 mL (11.28 mmol, 2 equiv) of 1M HCl. A light yellow precipitate was collected and extracted with dichloromethane and water. This procedure was adapted from a previously reported synthesis.[4] Yield: 44%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, J= 4.5 Hz, 4H, *a*), 7.69 (t, J= 8.0 Hz, 4H, *b*), 7.47 (td, J= 7.8, 1.9 Hz, 4H, *c*), 7.31 (td, J=7.4, 1.4Hz, 2H, *f*), 7.19 (td, J= 7.7, 1.6 Hz, 2H, *g*), 7.03 (dd, J= 7.5, 1.9 Hz, 2H, *e*), 7.02 (d, J= 7.5 Hz, 4H, *d*), 6.94 (br. s, 2H, O<u>H</u>), 6.78 (dd, J= 7.9, 1.2 Hz, 2H, *h*), 6.58 (s, 4H, *i*). For ^{1}H-NMR peak assignment of complexes made with ***p*-H_2L**, refer to Figure A1. In cases where all four pyridine arms are equivalent, a=a', etc.

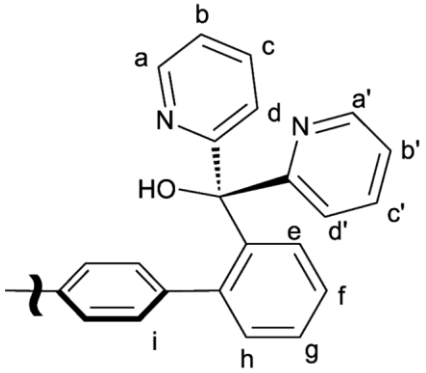


Figure A1. Proton assignments for complexes made with ***p*-H_2L**.

Synthesis of 1,3-bis(2-di(2'-pyridyl)hydroxymethylphenyl)benzene (*m*-H_2L): 1,3-bis(2-bromophenyl)benzene (prepared according to literature procedure[5]) (0.716g, 1.85 mmol, 1 equiv) was dissolved in Et_2O and frozen in a coldwell. 1.7 M ^{t}BuLi (4.45 mL solution in hexanes, 7.56 mmol, 4.1 equiv) were added dropwise to the thawing solution and allowed to react for 50 min warming to ambient temperature. A solution of di(2-pyridyl) ketone (0.71 g, 3.87 mmol, 2.1 equiv) in Et_2O was added dropwise. The reaction was allowed to run overnight and was subsequently quenched with 3.7 mL of 1M HCl. The golden biphasic solution was extracted with dichloromethane and washed with water and brine. Yield: 17%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, J=4.8 Hz, 4H, *a*), 7.66 (d, J=8.0 Hz, 4H, *d*), 7.45 (t, J=7.6 Hz, 4H, *b*), 7.31 (t, J=7.6 Hz, 2H, *f*), 7.17 (t, J=7.6 Hz, 2H, *g*), 7.06 (d, J=7.33 Hz, 2H, *e*), 6.99 (t, J=6.1 Hz, 4H, *c*), 6.87 (br. s, 2H, OH), 6.76 (s, 1H, *i*), 6.75 (d, J=7.6 Hz, 2H, *h*), 6.65 (d, 2H, *j*), 6.58 (d, J=6.3 Hz, 1H, *k*). For ^{1}H-NMR peak assignment of complexes made with ***m*-H_2L**, refer to Figure A2. In cases where all four pyridine arms are equivalent, a=a', etc.

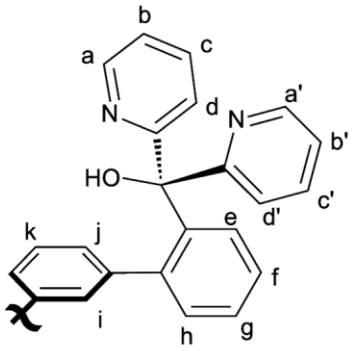


Figure A2. Proton assignments for complexes made with ***m*-H_2L**.

Synthesis of (2-di(2'-pyridyl)hydroxymethylphenyl)benzene (HL): 2-bromobiphenyl (0.75 g, 3.20 mmol, 1 equiv) was dissolved in THF and frozen in a coldwell. 1.7 M ^{t}BuLi (3.95 mL solution in pentane, 6.72 mmol, 2.1 equiv) were added dropwise to the thawing solution and allowed to react for 3 h warming to ambient temperature. A solution of di(2-pyridyl) ketone (0.88 g, 4.80 mmol, 1.5 equiv) in 15 mL THF was added dropwise. The reaction was allowed to run overnight and was subsequently quenched with 3.2 mL of 1M HCl. The golden biphasic solution was extracted with dichloromethane and washed with water and brine. Drying was performed over sodium sulfate and solid was recrystallized from acetone. Yield: 18%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (ddd, J= 4.9, 0.9 Hz, 2H, *a*), 7.67 (dt, J=8.0, 0.9 Hz, 2H, *b*), 7.46 (td, J=7.8, 1.8 Hz, 2H, *c*), 7.29 (td, J=7.4, 1.4 Hz,1H, *f*), 7.18 (td, J=7.6, 1.7 Hz, 1H, *g*), 7.11 (dd, J=7.4, 1.6, 1H, *e*), 7.02 (ddd, J=7.4, 4.9, 1.1 Hz, 2H, *d*), 6.99 (s, 1H, OH), 6.99-6.95 (m, 5H, *i, j, k*), 6.78 (dd, J=7.8, 1.0 Hz, 1H, *h*). For ^{1}H-NMR peak assignment of complexes made with **HL**, refer to Figure A3. In cases where all four pyridine arms are equivalent, a=a', etc.

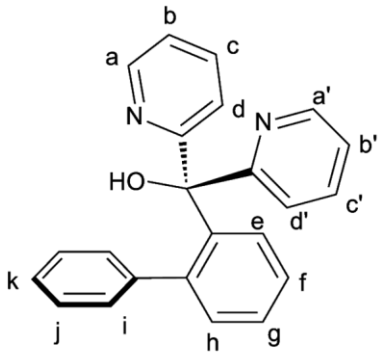


Figure A3. Proton assignments for complexes made with **HL**.

Synthesis of [*p*-H_2LCu(I)$_2$](2OTf): In the glovebox, an solution of (Cu(CF_3SO_3))$_2$·toluene (34.6 mg, .067 mmol, 1 equiv) in 5 mL acetonitrile was added dropwise at room temperature to a stirring suspension of ***p*-H_2L** (40 mg, .067 mmol, 1 equiv) in 10 mL acetonitrile. An immediate color change to bright yellow was accompanied by complete solubilization of the ligand. The solution was filtered through a glass-wool plug and crystals were grown from acetonitrile with liquid diffusion of diethyl ether. Yield: 85%. ^{1}H NMR (300 MHz, CD_3CN) δ 8.33 (br. s, 4H, *a*), 7.81 (br. s, 4H, *b*), 7.71 (br. s, 4H, *c*), 7.46 (t, J= 7.5 Hz, 2H, *f*), 7.29 (t, J= 7.7 Hz, 2H, *g*), 7.20 (br. s, 4H, *d*), 7.09 (d, J=7.4 Hz, 2H, *e*), 6.72 (d, J=8 Hz, 2H, *h*), 6.56 (br. s, 4H, *i*), 5.30 (br. s, 2H, O<u>H</u>). Anal. Calcd. for $C_{50}H_{42}Cu_2F_6N_8O_8S_2$: C, 50.54; H, 3.56; N, 9.43. Found: C, 49.07; H, 3.51; N, 7.10.

Synthesis of [*p*-H_2LCu(II)$_2$](4OTf): In the glovebox, a solution of Cu(CF_3SO_3)$_2$ (75.9 mg, .127 mmol, 1 equiv) in 5 mL acetonitrile was added dropwise at room temperature to a stirring suspension of ***p*-H_2L** (91.7 mg, .127 mmol, 1 equiv) in acetonitrile. Over the course of 15 minutes, a color change to dark blue was accompanied by complete solubilization of the ligand. After 20 additional minutes of stirring, the blue solution was filtered through a glass-wool plug and purified by repeated precipitation with diethyl ether. Yield: 95%. ^{1}H NMR (300 MHz, CD_3CN) δ 9.78 (br. s), 8.52 (br. s).

Synthesis of [*p*-LCu(II)$_2$]$_2$(4OTf): In the glovebox, sodium hexamethyldisilazide (NaHMDS) (24.4 mg, .133 mmol, 2 equiv) was dissolved in 5 mL THF and added dropwise to a room-temperature solution of ***p*-H_2L** (39.8 mg, .067 mmol, 1 equiv) in 5 mL THF while stirring vigorously. The reaction was allowed to proceed for 15 min, then exposed to reduced pressure for 1 h. The resulting tan-colored deprotonated ligand was re-dissolved in 10 mL acetonitrile and stirred vigorously as Cu(CF_3SO_3)$_2$ (48.1 mg, .133 mmol, 1 equiv) in 5 mL acetonitrile was added. An immediate color change to dark green was observed. The solution was allowed to stir for 30 min and filtered through a glass-wool plug. The complex was purified via recrystallization from acetonitrile and diethyl ether liquid diffusion. The same product may be obtained by reaction of the **[*p*-H_2LCu(I)$_2$](2OTf)** complex with excess O_2 or H_2O_2 in acetonitrile (confirmed by ^{1}H-NMR and crystal structure). The O_2 reaction requires on the order of 4 days to reach completion while the H_2O_2 reaction proceeds almost instantaneously. Yield: 15%. UV-Vis (CH_3CN, λ_{max} (ε)): 257 (31,300 M^{-1} cm^{-1}), 731 (147 M^{-1} cm^{-1}) nm. ^{1}H NMR (300 MHz, CD_3CN) δ 158.52 (s), 71.81 (s), 57.35 (s), 38.12 (s), 34.87 (s), 19.07 (s), 16.66 (s), 11.76 (s), 10.10 (s), 9.76 (s).

Synthesis of [*m*-H_2LCu(I)$_2$](2OTf): (Cu(CF_3SO_3))$_2$·toluene (34.6 mg, .067 mmol, 1 equiv) was dissolved in 5 mL acetonitrile and added dropwise at room temperature to a vigorously stirring suspension of ***m*-H_2L** (40 mg, .067 mmol, 1 equiv) in 10 mL acetonitrile. An immediate color change to bright yellow was accompanied by complete solubilization of the ligand. Purification was achieved by filtration through a glass-wool plug and repeated precipitation of the complex with diethyl ether. Yield: 82%. ^{1}H NMR (300 MHz, CD_3CN) δ 8.30 (br. s, 4H, *a*), 7.96 (br. s, 1H, *i*), 7.76 (br. s, 4H, *c*), 7.63 (br. s, 4H, *d*), 7.49 (t, J=7.2 Hz, 2H, *f*), 7.29 (t, J=7.3 Hz, 2H, *g*), 7.16 (br. s, 4H, *b*), 7.09 (br. s, 2H, *e*), 6.89 (br. s, 1H, *k*), 6.72 (d, J= 8.0Hz, 2H, *h*), 6.52 (br. s, 2H, *j*), 5.33 (br. s, 2H, O<u>H</u>).

Synthesis of [*m*-H_2LCu(II)$_2$](4OTf): Cu(CF_3SO_3)$_2$ (49 mg, .136 mmol, 2 equiv) was dissolved in 5 mL acetonitrile and added dropwise at room temperature to a vigorously stirring suspension of ***m*-H_2L** (40 mg, .068 mmol, 1 equiv) in 10 mL acetonitrile. An immediate color change to violet and then dark blue was accompanied by complete solubilization of ligand. Crystals were grown from liquid diffusion of diethyl ether into acetonitrile. Yield: 15%. UV-Vis (CH_3CN, λ_{max} (ε)): 262 (15,700 M^{-1} cm^{-1}), 615 (78 M^{-1} cm^{-1}) nm. ^{1}H NMR (300 MHz, CD_3CN) δ 9.88 (br. s), 8.33 (br. s), 6.26 (br. s).

Synthesis of [*m*-LCu(II)$_2$]$_3$(6OTf): In the glovebox, NaHMDS (24.5 mg, .134 mmol, 2 equiv) was dissolved in 5 mL THF and added dropwise to a room-temperature solution of ***m*-H_2L** (40.0 mg, .067 mmol, 1 equiv) in 5 mL THF while stirring vigorously. The reaction was allowed to proceed for 30 min, then exposed to reduced pressure for 1 h. The resulting tan-colored ***m*-L** was re-dissolved in 10 mL acetonitrile and stirred vigorously as Cu(CF_3SO_3)$_2$ (48.3 mg, .134 mmol, 1 equiv) in 5 mL acetonitrile was added. An immediate color change to dark green was observed. The

solution was allowed to proceed overnight, then filtered through a glass-wool plug. The complex was purified via recrystallization from acetonitrile and diethyl ether liquid diffusion to give blue crystals. The same product may be obtained by reaction of the **[*m*-H_2LCu(I)$_2$](2OTf)** complex with excess O_2 or H_2O_2 in acetonitrile (confirmed by ^{1}H-NMR). The O_2 reaction requires on the order of 5 days to reach completion while the H_2O_2 reaction proceeds almost instantaneously. Yield: 19%. ^{1}H NMR (300 MHz, CD_3CN) δ 82.33, 78.64, 75.21, 73.05, 70.64, 56.19, 54.64, 52.92, 51.64, 50.09, 46.82, 38.80, 37.85, 36.73, 36.03, 35.04, 34.28, 33.66, 31.77, 31.08, 30.65, 21.94, 21.72, 20.77, 20.56, 12.11, 11.69, 11.28, 9.72, 9.28, 8.88, 8.05, 7.36, 6.85, 6.50, 6.14.

Synthesis of [HLCu(I)](OTf): ($Cu(CF_3SO_3)$)$_2$·toluene (38 mg, .074 mmol, 1 equiv) was dissolved in 5 mL acetonitrile and added dropwise at room temperature to a vigorously stirring suspension of **HL** (50 mg, .148 mmol, 2 equiv) in 10 mL acetonitrile. An immediate color change to bright yellow was accompanied by complete solubilization of the ligand. Purification was achieved by filtration through a glass-wool plug and repeated precipitation of the complex with diethyl ether. Yield: 63%. ^{1}H NMR (300 MHz, CD_3CN) δ ^{1}H NMR 8.23 (br. s, 2H, *a*), 7.82 (d, *J* = 7.4 Hz, 2H, *d*), 7.64 (t, *J* = 7.5 Hz, 2H, *b*), 7.39 (ddd, *J* = 7.5, 4.4, 1.1 Hz, 1H, *f*), 7.28 (td, *J* = 7.7, 1.6 Hz, 1H, *g*), 7.17 (br. t, J=6.2 Hz, 2H, *c*), 7.10 (dd, *J* = 7.5, 1.4 Hz, 1H, *e*), 7.07 – 6.93 (m, 5H, *i*, *j*, *k*), 6.75 (dd, *J* = 7.9, 1.3 Hz, 1H, *h*), 5.30 (s, 1H, O<u>H</u>).

Synthesis of [HLCu(II)](2OTf): $Cu(CF_3SO_3)_2$ (53.4 mg, .148 mmol, 1 equiv) was dissolved in 5 mL acetonitrile and added dropwise at room temperature to a vigorously stirring suspension of **HL** (50 mg, .148 mmol, 1 equiv) in 10 mL acetonitrile. An immediate color change to lavender and then dark blue was accompanied by complete solubilization of ligand. Crystals were grown from liquid diffusion of diethyl ether into acetonitrile. Yield: 13%. ^{1}H NMR (300 MHz, CD_3CN) δ 9.85, 9.28, 8.49, 7.42, 7.23, 6.29. Anal. Calcd. for $C_{29}H_{24}CuF_6N_4O_7S_2$: C, 44.53; H, 3.09; N, 7.16. Found: C, 41.37; H, 3.22; N, 4.04.

Synthesis of [LCu(II)]$_2$(2OTf)/[LCu(II)]$_3$(3OTf): In the glovebox, NaHMDS) (54 mg, .296 mmol, 1 equiv) was dissolved in 15 mL THF and added dropwise to a room-temperature solution of **HL** (100 mg, .296 mmol, 1 equiv) in 20 mL THF while stirring vigorously. The reaction was allowed to proceed for 50 min, then exposed to reduced pressure for 1 h. The resulting light-blue deprotonated ligand was re-dissolved in 15 mL acetonitrile and stirred vigorously as $Cu(CF_3SO_3)_2$ (107 mg, .296 mmol, 1 equiv) in 15 mL acetonitrile was added. An immediate color change to dark green was observed. The solution was allowed to stir for 30 min and filtered through a glass-wool plug. Crystals of both complexes were grown from acetonitrile and diethyl ether liquid diffusion; **LCu(II)]$_2$(2OTf)** is green and **[LCu(II)]$_3$(3OTf)** is teal/blue . The same product may be obtained by reaction of the **[HLCu(I)](OTf)** complex with excess O_2 or H_2O_2 in acetonitrile (confirmed by ^{1}H-NMR). The O_2 reaction requires on the order of 5 days to reach completion while the H_2O_2 reaction proceeds almost instantaneously. Yield: 22%. ^{1}H NMR (600 MHz, CD_3CN) δ 164.95 (s, 1H), 73.29 (s, 1H), 64.18 (s, 1H), 39.92 (s, 1H), 39.14 (s, 1H), 20.80 (s, 1H), 16.42 (s, 1H), 14.22 (s, 1H), 11.42 (s, 1H), 11.06 (s, 1H), 10.01 (s, 1H), 9.28 (s, 1H), 8.01 (s, 1H), 6.50 (s, 1H), 3.94 (s, 1H), 1.42 (s, 1H), 0.99 (s, 1H). Anal. Calcd. for $C_{56}H_{54}Cu_2F_6N_6O_8S_2$: C, 54.06; H, 4.37; N, 6.75. Found: C, 50.75; H, 3.60; N, 6.04.

Nuclear Magnetic Resonance Spectra

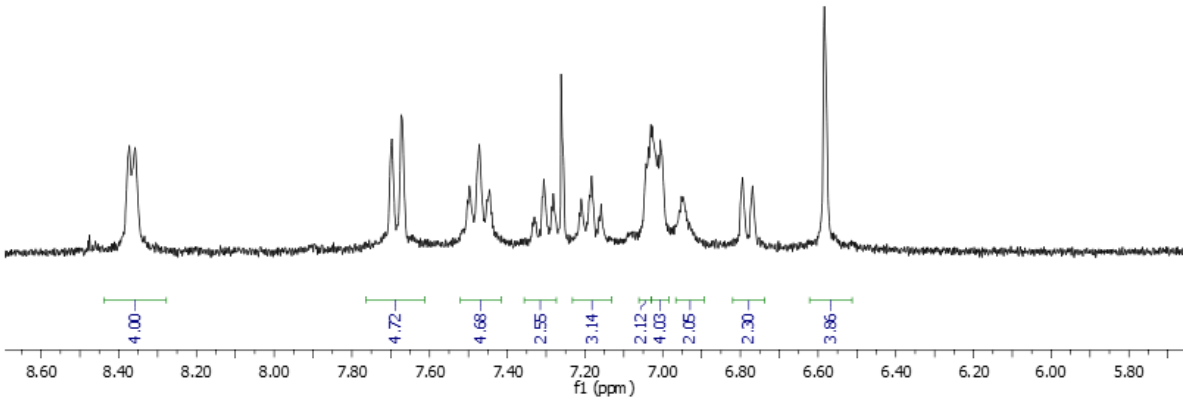


Figure A4. ^{1}H NMR (300 MHz, 25°, $CDCl_3$) of ***p*-H_2L**. Solvent peaks have been omitted.

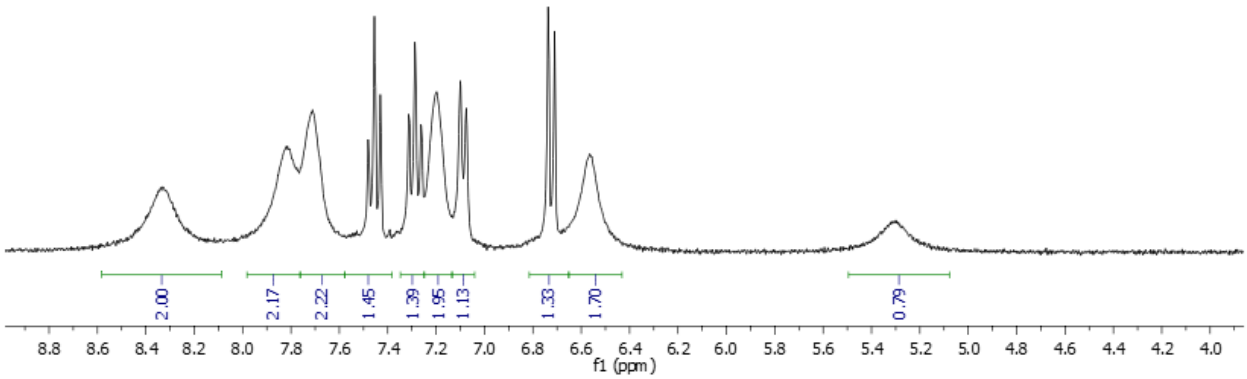


Figure A5. ^{1}H NMR (300 MHz, 25°, CD_3CN) of **[*p*-H_2LCu(I)$_2$](2OTf)**. Solvent peaks have been omitted.

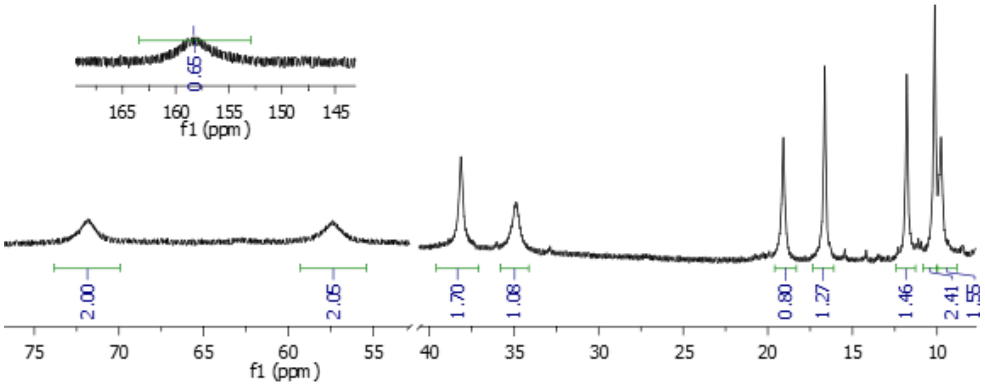


Figure A6. ^{1}H NMR (600 MHz, 25°, CD_3CN) of **[*p*-LCu(II)$_2$]$_2$(4OTf)**. Solvent peaks have been omitted.

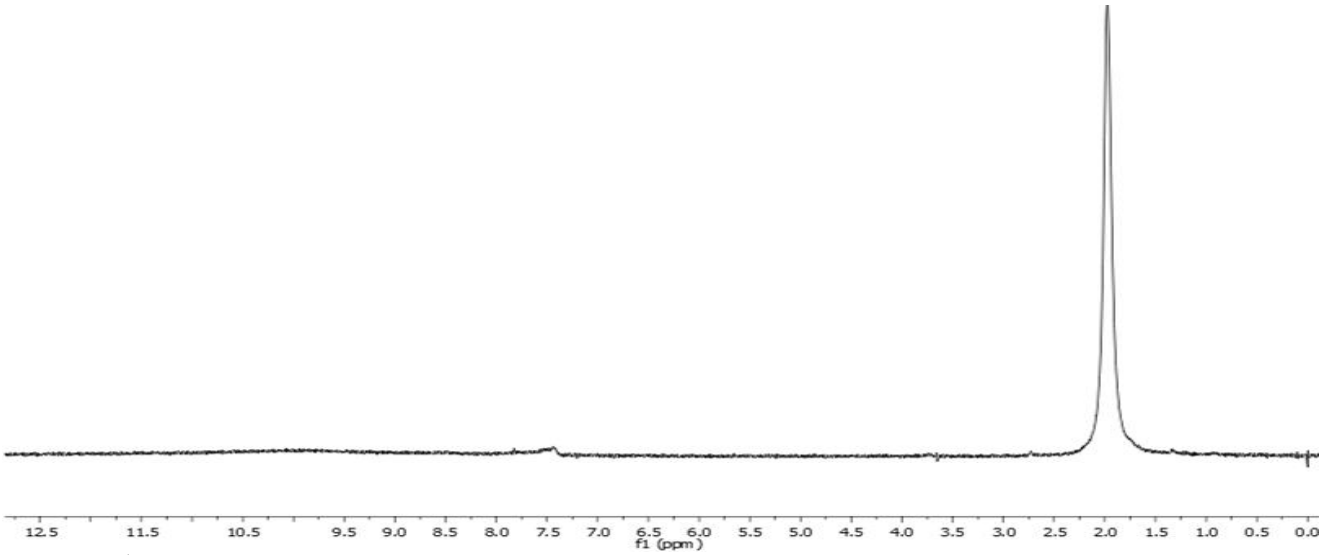


Figure A7. ^{1}H NMR (300 MHz, 25°, CD_3CN) of **[*p*-H_2LCu(II)$_2$](4OTf)**.

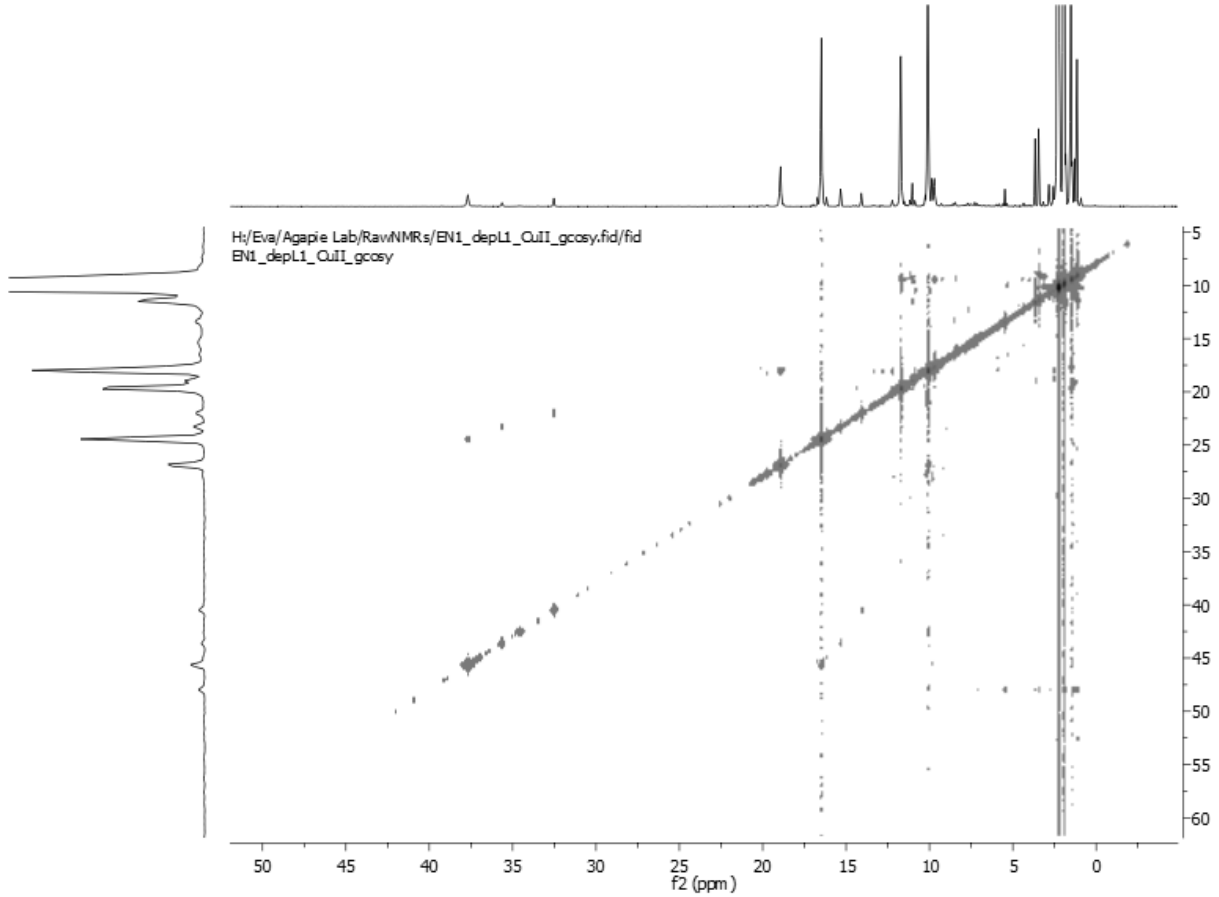


Figure A8. gCOSY experiment (600 MHz, 25°, CD_3CN) of **[*p*-LCu(II)$_2$]$_2$(4OTf)**.

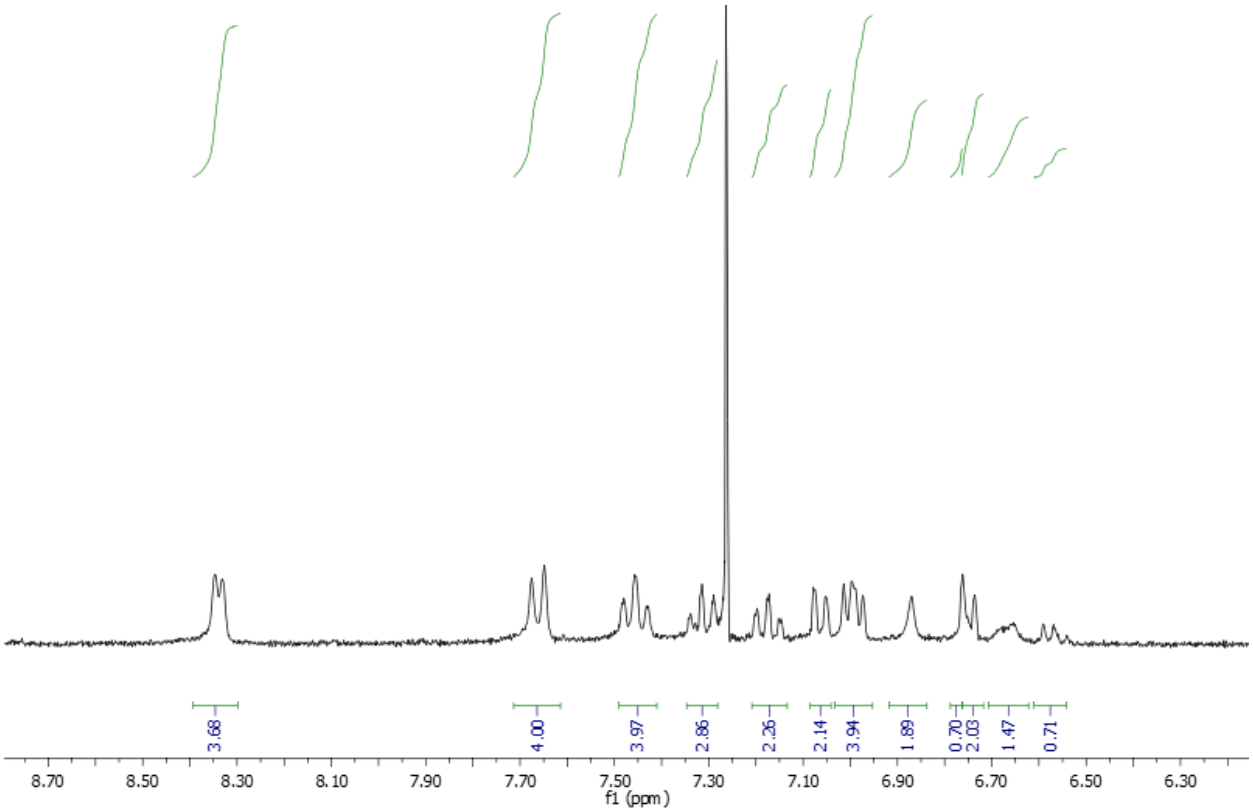


Figure A9. ^{1}H NMR (300 MHz, 25°, $CDCl_3$) of ***m*-H_2L**. Solvent peaks have been omitted.

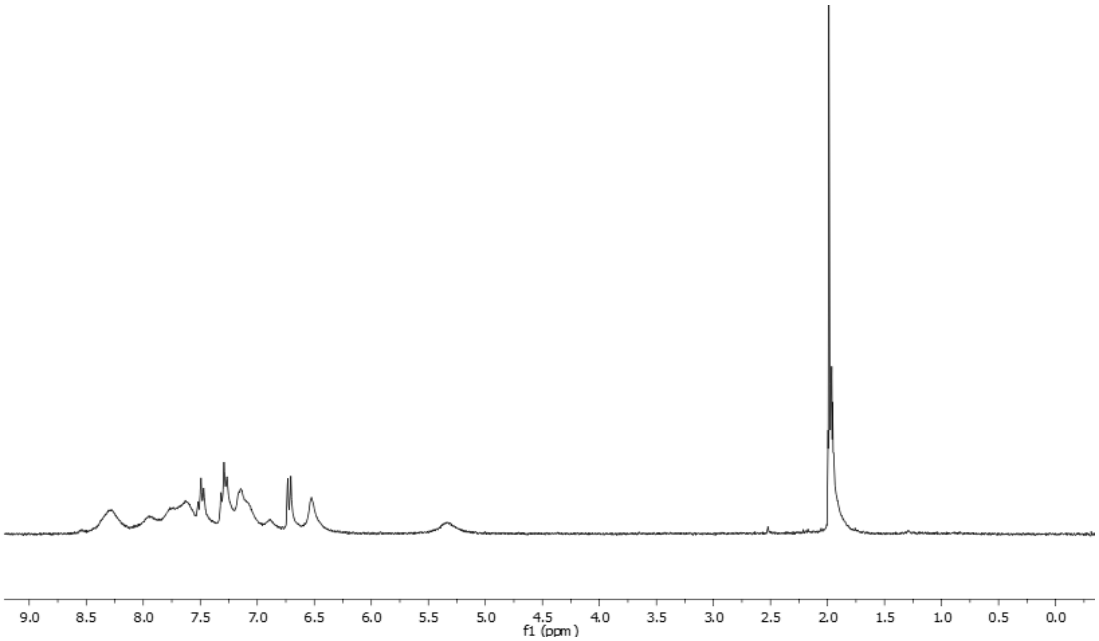


Figure A10. ^{1}H NMR (300 MHz, 25°, CD_3CN) of **[*m*-H_2LCu(I)$_2$](2OTf)**.

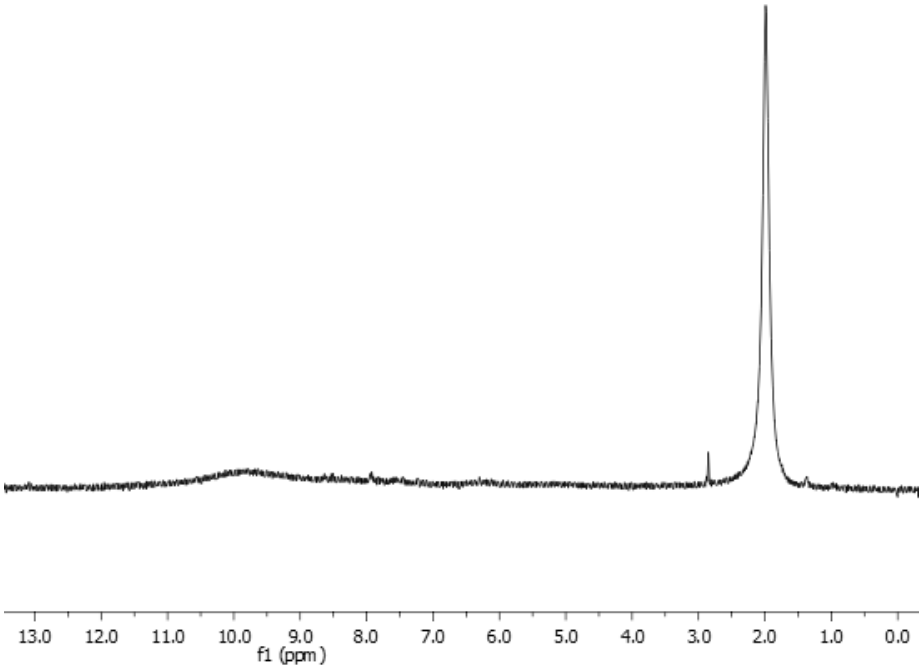


Figure A11. ^{1}H NMR (300 MHz, 25°, CD_3CN) of **[*m*-H_2LCu(II)$_2$](4OTf)**.

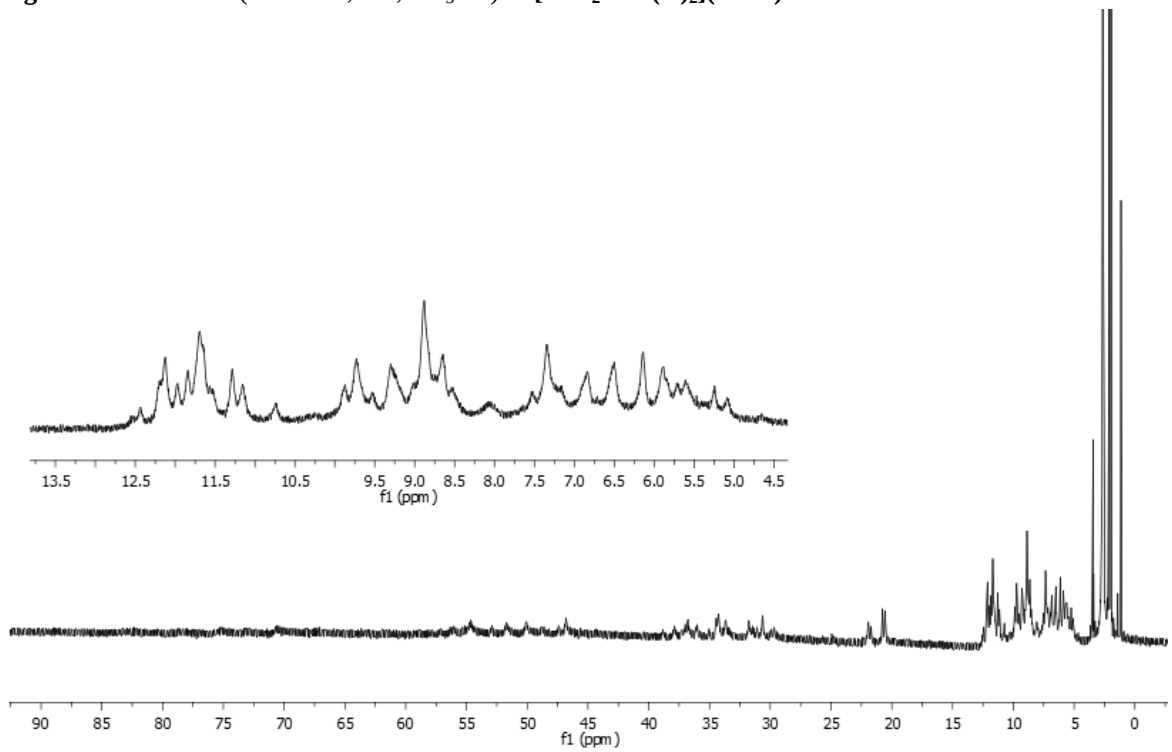


Figure A12. ^{1}H NMR (300 MHz, 25°, CD_3CN) of **[*m*-LCu(II)$_2$]$_3$(6OTf)**.

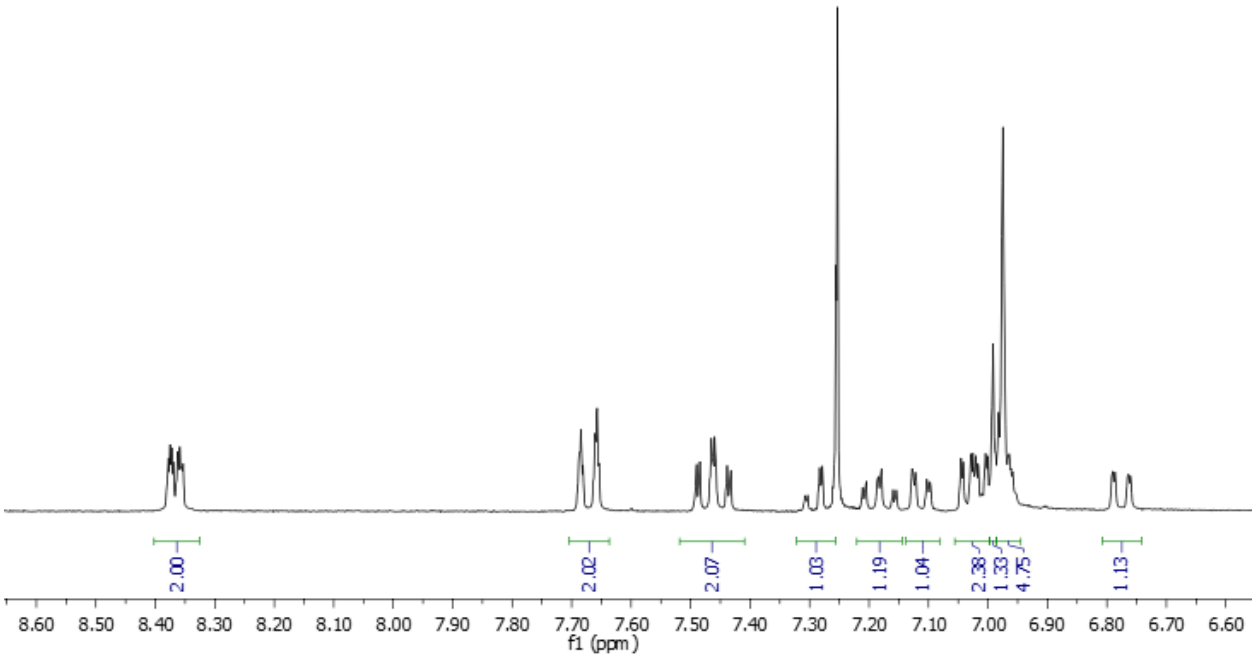


Figure A13. ^{1}H NMR (300 MHz, 25°, $CDCl_3$) of **HL**. Solvent peaks have been omitted.

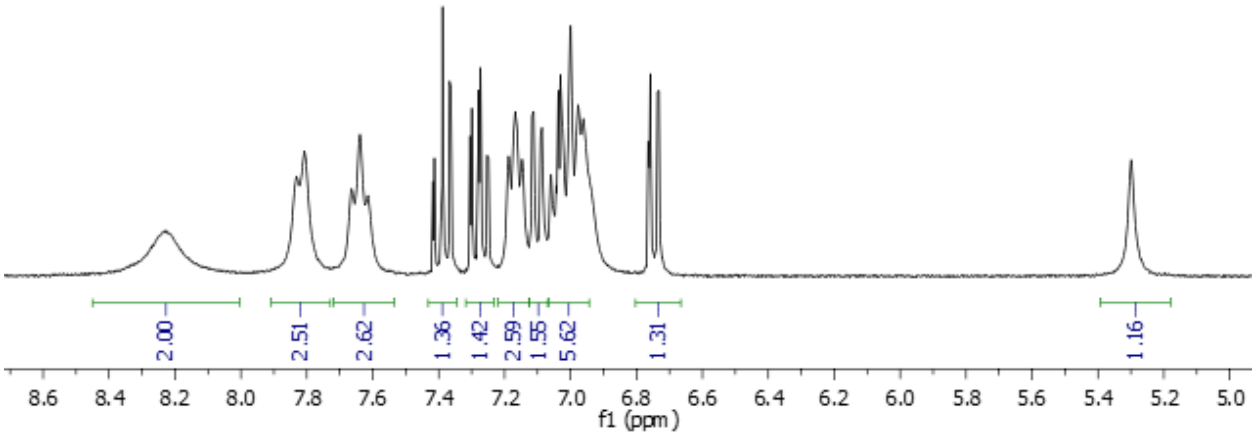


Figure A14. ^{1}H NMR (300 MHz, 25°, CD_3CN) of **[HLCu(I)](OTf)**. Solvent peaks have been omitted.

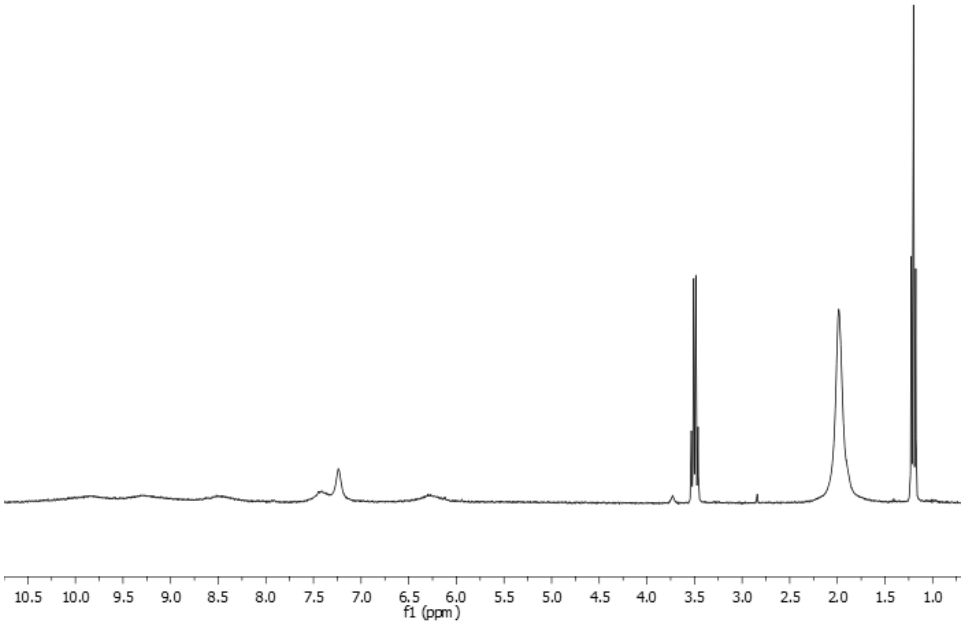


Figure A15. ^{1}H NMR (300 MHz, 25°, CD_3CN) of **[HLCu(II)](2OTf)**.

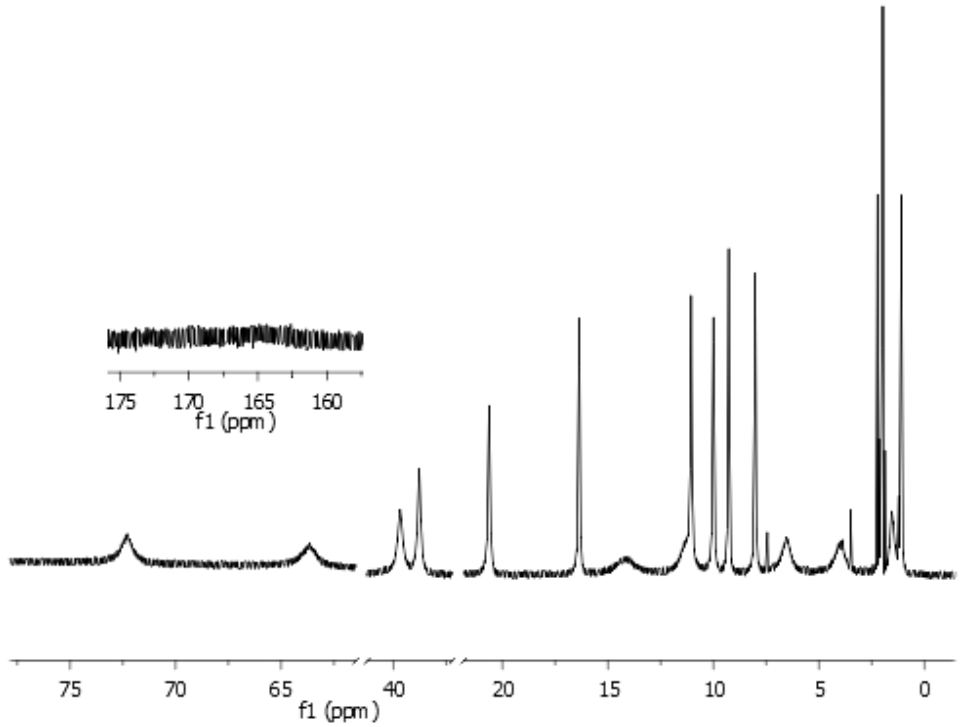


Figure A16. ^{1}H NMR (600 MHz, 25°, CD_3CN) of **[LCu(II)]$_2$(2OTf)**.

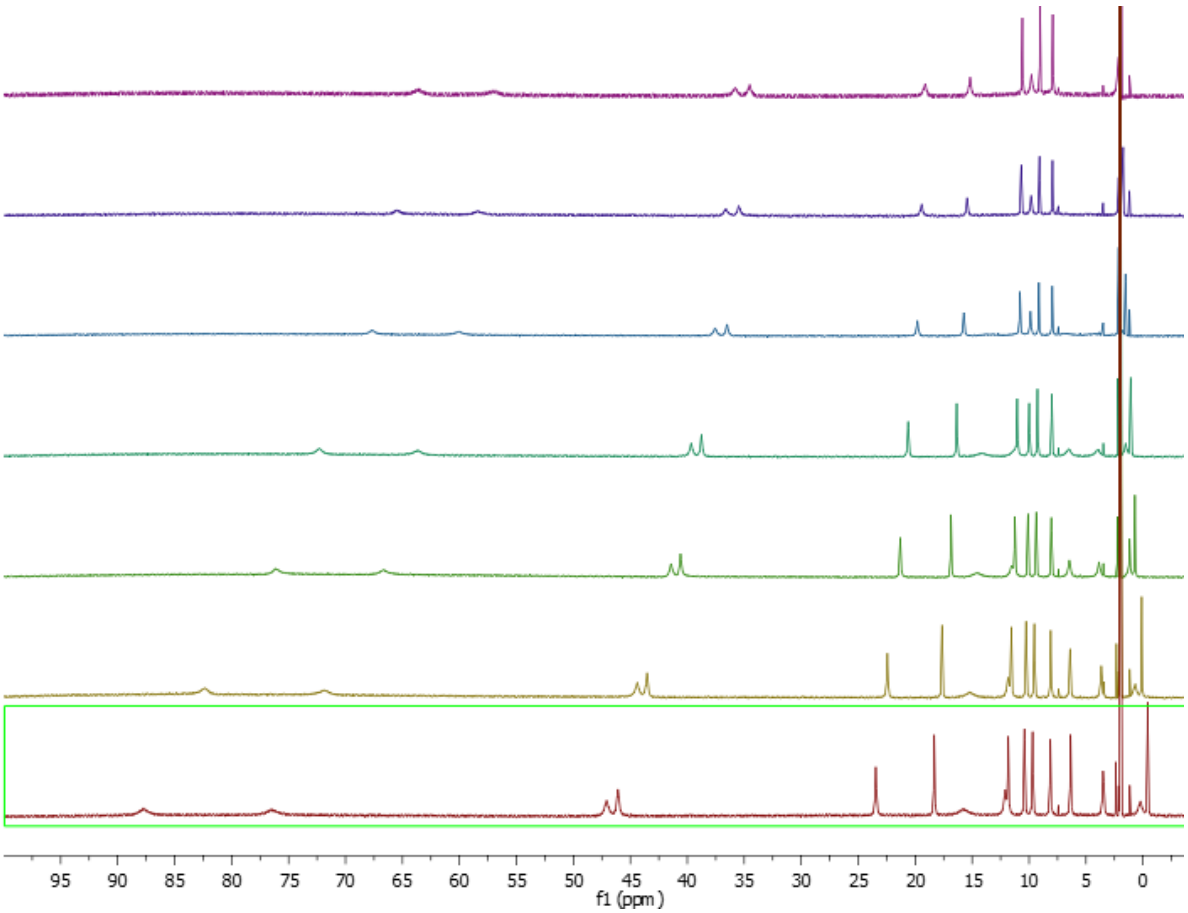


Figure A17. Variable Temperature (VT) ^{1}H NMR (600 MHz, -25°-65°, CD_3CN) of **[LCu(II)]$_2$(2OTf)**. Temperatures are, top to bottom, 65°C, 55°C, 45°C, 35°C, 25°C, 10°C, -10°C, -25°C.

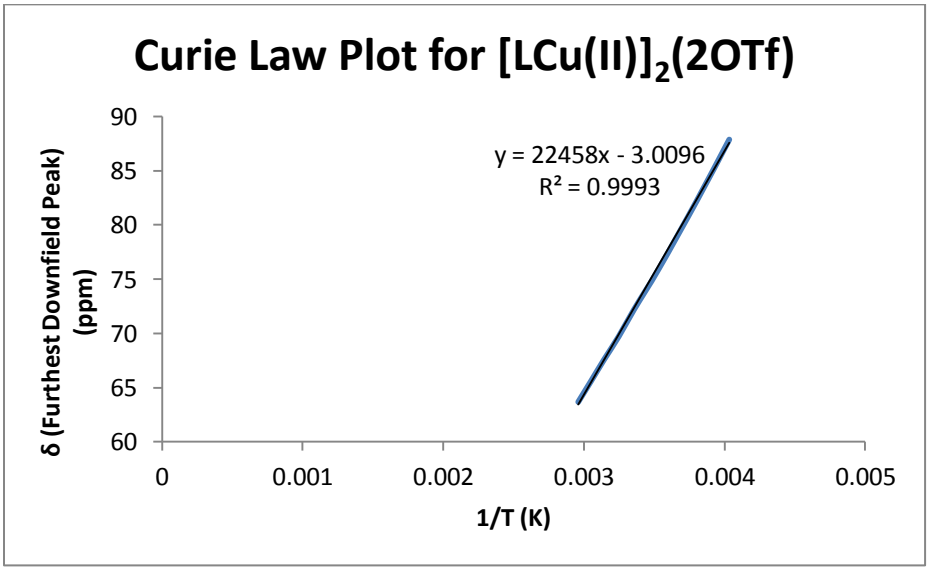


Figure A18. Curie Law plot for **[LCu(II)]$_2$(2OTf)** based on VT-NMR data (see **Figure A16**).

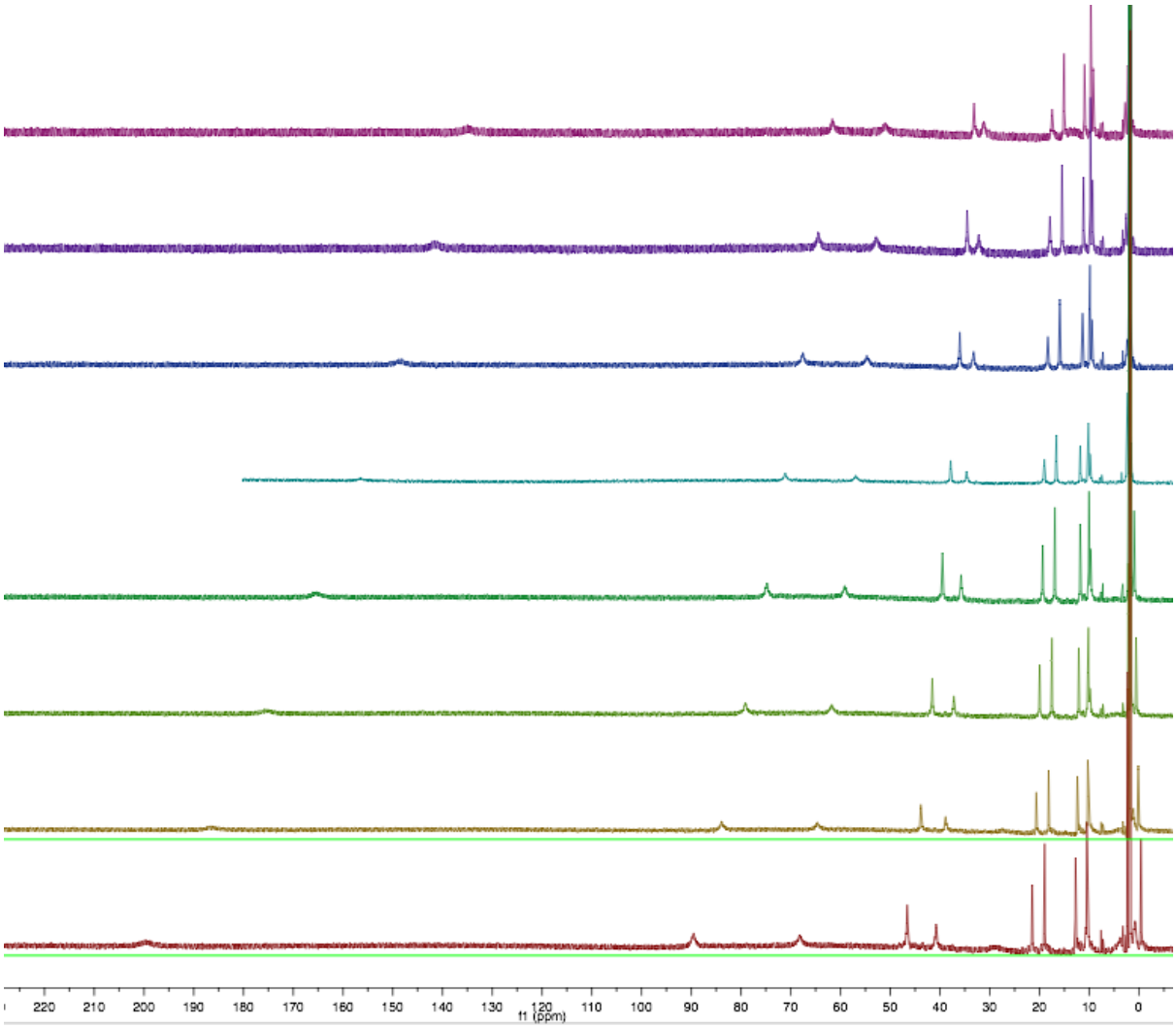


Figure A19. Variable Temperature (VT) ^{1}H NMR (600 MHz, -25°-65°, CD_3CN) of **[*p*-LCu(II)$_2$]$_2$ (4OTf)**. Temperatures are, top to bottom, 70°C, 55°C, 40°C, 25°C, 10°C, -5°C, -20°C, -35°C.

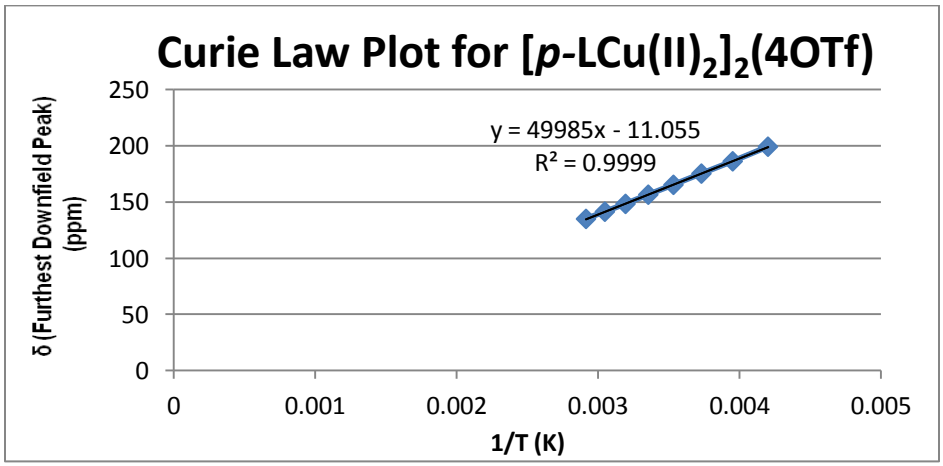


Figure A20. Curie Law plot for **[*p*-LCu(II)$_2$]$_2$(4OTf)** based on VT-NMR data (see **Figure A19**).

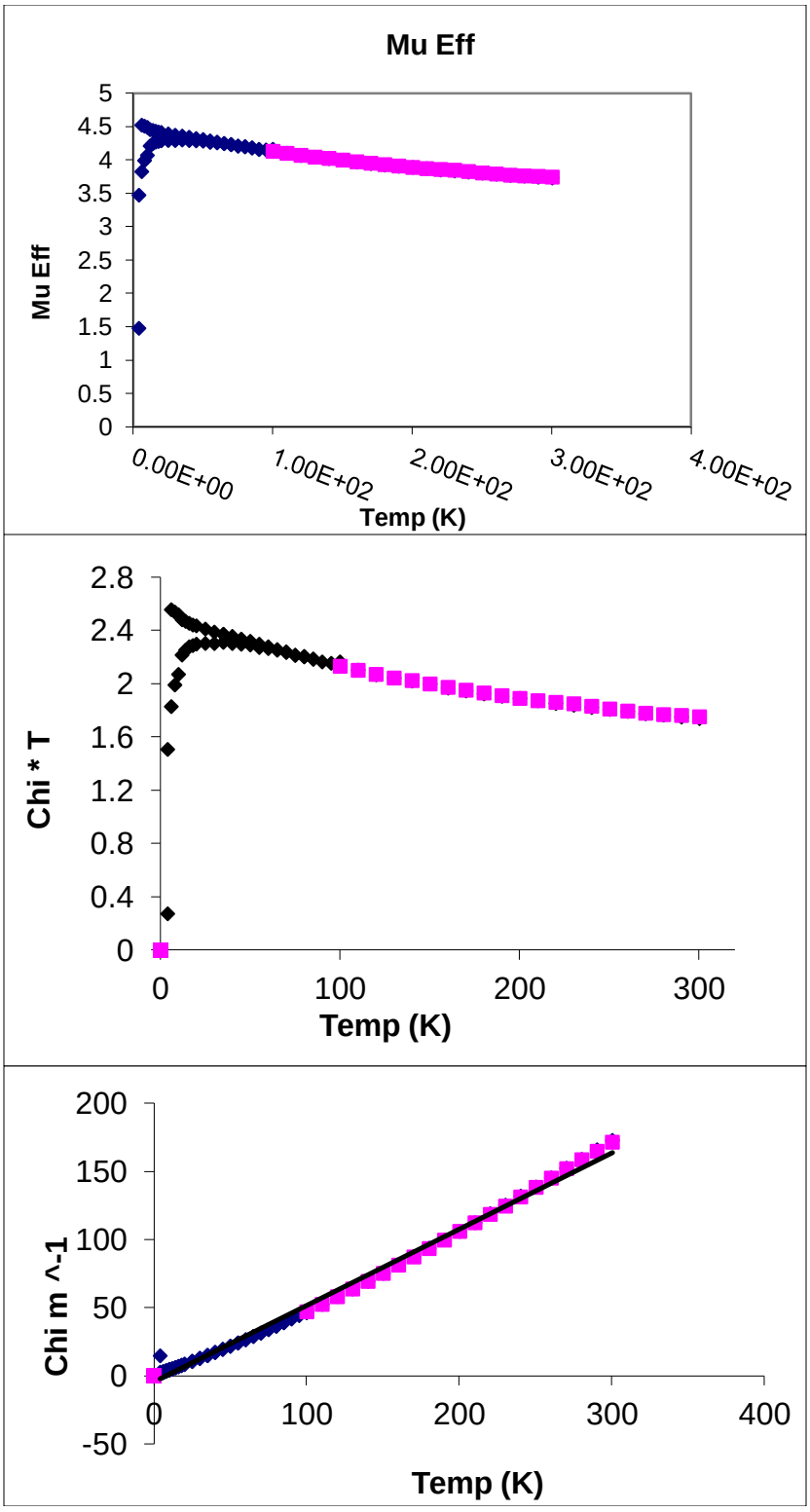


Figure A21. SQUID Magnetometry data for **[*p*-LCu(II)$_2$]$_2$(4OTf)**.

Crystallographic Data

Table A1. Crystal and refinement data for **[*p*-H_2LCu(I)$_2$](2OTf)**.

Empirical formula	$[C_{48}H_{42}N_8O_2Cu_2]^{+2}$ $2[CF_3O_3S]^-$ • C $H_3C{\equiv}N$	
Formula weight	1229.17	
Crystallization Solvent	Toluene/acetonitrile	
Crystal Habit	Plate	
Crystal size	0.36 x 0.23 x 0.07 mm^3	
Crystal color	Colorless	
	Data Collection	
Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKa	
Data Collection Temperature	100(2) K	
q range for 9928 reflections used in lattice determination	2.59 to 29.55°	
Unit cell dimensions	a = 10.9827(5) Å	a= 65.918(3)°
	b = 11.4038(6) Å	b= 73.507(3)°
	c = 12.1961(6) Å	g = 76.655(3)°
Volume	1325.58(11) Å^3	
Z	1	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.540 Mg/m^3	
F(000)	628	
q range for data collection	1.95 to 29.55°	
Completeness to q = 29.55°	93.4 %	
Index ranges	$-15 \le h \le 15$, $-15 \le k \le 15$, $-16 \le l \le 16$	
Data collection scan type	ω scans; 11 settings	
Reflections collected	23416	
Independent reflections	6922 [R_{int}= 0.0403]	
Absorption coefficient	0.965 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.6364	
	Structure solution and Refinement	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Geometric positions	
Structure refinement program	SHELXL-97 (Sheldrick, 2008)	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	6922 / 0 / 447	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	2.096	
Final R indices [I>2s(I), 4837 reflections]	R1 = 0.0523, *w*R2 = 0.0727	
R indices (all data)	R1 = 0.0889, *w*R2 = 0.0753	
Type of weighting scheme used	Sigma	

Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.735 and -0.782 e.Å^{-3}

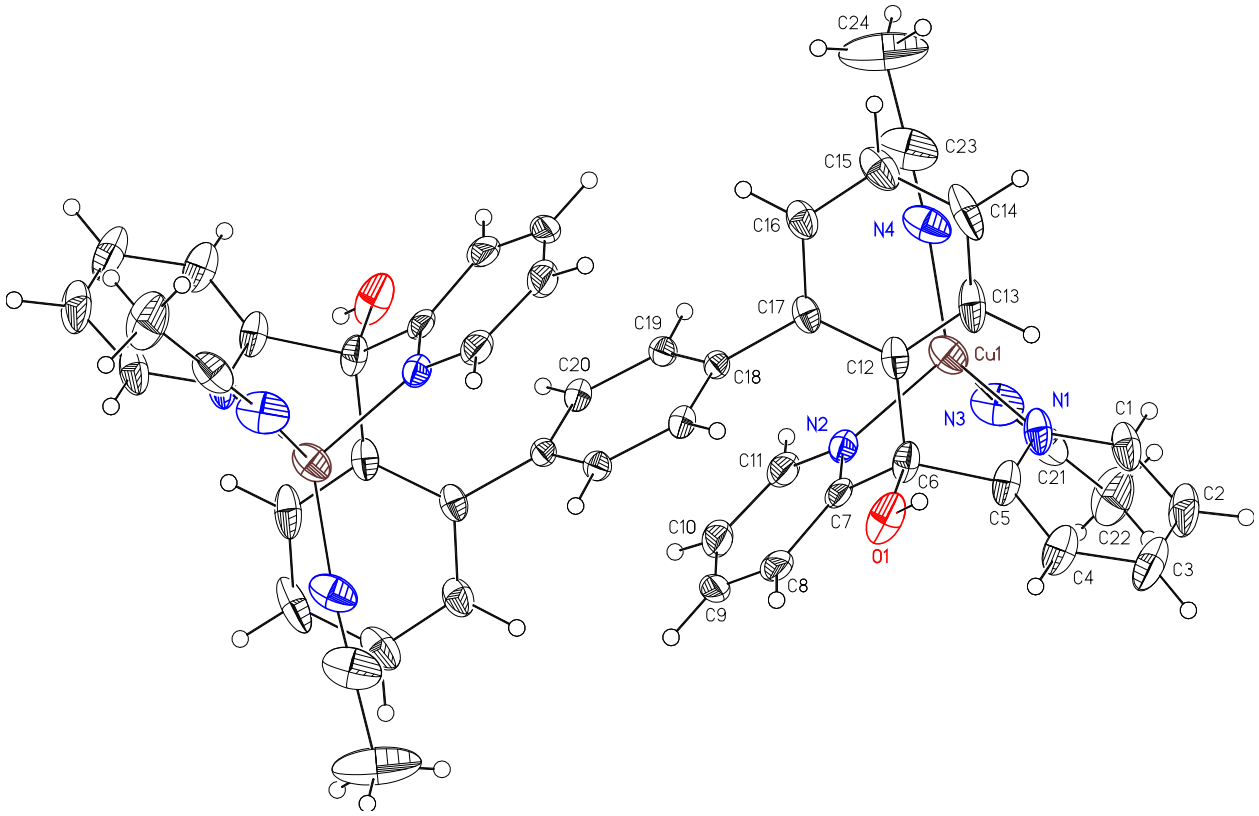


Figure A21. Structural drawing of **[*p*-H_2LCu(I)$_2$](2OTf)** with 50% thermal probability ellipsoids.

Special Refinement Details for [*p*-H_2LCu(I)$_2$](2OTf). Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. The molecule sits at a center of symmetry so application of that symmetry generates the chemically unique moiety from the asymmetric. There is disorder in this crystal manifested as two unique orientations of the triflate anion. Additional disorder occurs in the acetonitrile group, which also sits at a center of symmetry. Disorder was modeled without geometric restraints, however the total occupancy of the triflate site was constrained to one and the occupancy of the acetonitrile was constrained to one-half. Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

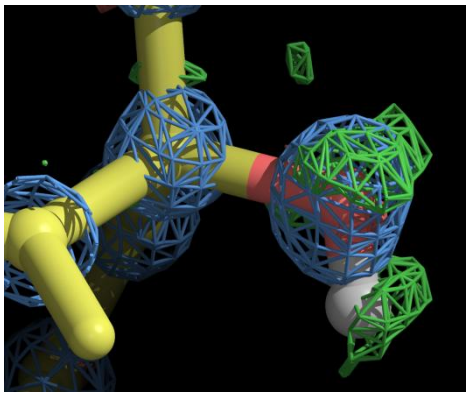


Figure A22. Electron density around the OH group. Green nets indicate difference (F_o-F_c) density and blue nets indicate observed ($F_o\phi_c$)density. Hydrogen atoms were excluded from the calculation.

Table A2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **[*p*-H_2LCu(I)$_2$](2OTf)** (CCDC 731671). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Cu(1)	-112(1)	5996(1)	6651(1)	29(1)	1
O(1)	3238(2)	7941(2)	6290(2)	39(1)	1
N(1)	-158(2)	7564(2)	7083(2)	28(1)	1
N(2)	1399(2)	6557(2)	5212(2)	21(1)	1
N(3)	-1641(2)	6781(2)	5795(2)	40(1)	1
N(4)	-55(2)	4247(2)	7757(2)	35(1)	1
C(1)	-1284(2)	8238(3)	7418(2)	34(1)	1
C(2)	-1381(2)	9416(3)	7500(2)	42(1)	1
C(3)	-289(3)	9962(3)	7192(3)	46(1)	1
C(4)	888(2)	9291(2)	6845(2)	37(1)	1
C(5)	917(2)	8095(2)	6813(2)	28(1)	1
C(6)	2209(2)	7276(2)	6479(2)	25(1)	1
C(7)	2269(2)	7196(2)	5239(2)	21(1)	1
C(8)	3172(2)	7758(2)	4198(2)	31(1)	1
C(9)	3217(2)	7606(2)	3117(2)	37(1)	1
C(10)	2352(2)	6919(2)	3095(2)	35(1)	1
C(11)	1453(2)	6430(2)	4153(2)	27(1)	1
C(12)	2339(2)	5934(2)	7506(2)	22(1)	1
C(13)	1673(2)	5752(3)	8703(2)	33(1)	1
C(14)	1777(2)	4573(3)	9666(2)	40(1)	1
C(15)	2566(2)	3524(3)	9430(2)	35(1)	1
C(16)	3258(2)	3685(2)	8256(2)	27(1)	1
C(17)	3200(2)	4874(2)	7285(2)	21(1)	1
C(18)	4104(2)	4968(2)	6089(2)	17(1)	1
C(19)	3921(2)	4405(2)	5344(2)	18(1)	1
C(20)	4791(2)	4448(2)	4264(2)	19(1)	1
C(21)	-2491(2)	7532(3)	5513(2)	32(1)	1
C(22)	-3580(2)	8503(3)	5161(3)	51(1)	1
C(23)	123(3)	3210(3)	8403(3)	47(1)	1

C(24)	355(3)	1861(3)	9236(3)	85(1)	1
S(31A)	2962(1)	9190(1)	8946(1)	29(1)	0.531(2)
F(31A)	5184(3)	8392(3)	9537(4)	62(1)	0.531(2)
F(32A)	4717(3)	10446(3)	8808(4)	71(1)	0.531(2)
F(33A)	5288(5)	9350(8)	7563(6)	73(2)	0.531(2)
O(31A)	2529(7)	9185(5)	10175(6)	50(2)	0.531(2)
O(32A)	2520(4)	10349(4)	8014(4)	38(1)	0.531(2)
O(33A)	3021(3)	8036(3)	8757(4)	38(1)	0.531(2)
C(31A)	4587(7)	9340(7)	8764(7)	51(2)	0.531(2)
S(31B)	4276(2)	9252(2)	8055(2)	37(1)	0.469(2)
F(31B)	4377(5)	7812(5)	10297(4)	90(2)	0.469(2)
F(32B)	2447(6)	8457(10)	9937(7)	171(4)	0.469(2)
F(33B)	3488(9)	9782(8)	10037(6)	181(5)	0.469(2)
O(31B)	3436(7)	10357(5)	7520(5)	84(2)	0.469(2)
O(32B)	4214(6)	8126(4)	7871(5)	79(2)	0.469(2)
O(33B)	5497(11)	9526(12)	7963(11)	97(4)	0.469(2)
C(31B)	3711(8)	8843(12)	9640(7)	94(4)	0.469(2)
N(41)	6021(5)	5992(5)	8236(5)	61(2)	0.50
C(42)	5408(9)	5582(6)	9195(8)	39(2)	0.50
C(43)	4625(8)	5111(8)	10417(7)	46(2)	0.50

Table A3. Selected bond lengths [Å] and angles [°] for **[*p*-H_2LCu($I)_2$](2OTf)** (CCDC 731671).

Cu(1)-N(4)	1.897(2)	N(4)-Cu(1)-N(2)	119.54(8)
Cu(1)-N(2)	2.0406(19)	N(4)-Cu(1)-N(1)	125.66(8)
Cu(1)-N(1)	2.046(2)	N(2)-Cu(1)-N(1)	90.79(8)
Cu(1)-N(3)	2.0615(19)	N(4)-Cu(1)-N(3)	117.95(8)
		N(2)-Cu(1)-N(3)	101.75(8)
		N(1)-Cu(1)-N(3)	95.11(8)

Table A4. Bond lengths [Å] and angles [°] for **[*p*-H_2LCu($I)_2$](2OTf)** (CCDC 731671).

Cu(1)-N(4)	1.897(2)	C(1)-C(2)	1.364(4)
Cu(1)-N(2)	2.0406(19)	C(2)-C(3)	1.366(4)
Cu(1)-N(1)	2.046(2)	C(3)-C(4)	1.390(3)
Cu(1)-N(3)	2.0615(19)	C(4)-C(5)	1.373(3)
O(1)-C(6)	1.418(3)	C(5)-C(6)	1.556(3)
N(1)-C(5)	1.347(3)	C(6)-C(7)	1.533(3)
N(1)-C(1)	1.349(3)	C(6)-C(12)	1.539(3)
N(2)-C(11)	1.340(3)	C(7)-C(8)	1.386(3)
N(2)-C(7)	1.343(3)	C(8)-C(9)	1.385(3)
N(3)-C(21)	1.138(3)	C(9)-C(10)	1.376(3)
N(4)-C(23)	1.130(3)	C(10)-C(11)	1.376(3)

C(12)-C(13)	1.387(3)
C(12)-C(17)	1.421(3)
C(13)-C(14)	1.385(3)
C(14)-C(15)	1.388(3)
C(15)-C(16)	1.376(3)
C(16)-C(17)	1.392(3)
C(17)-C(18)	1.492(3)
C(18)-C(19)	1.385(3)
C(18)-C(20)#1	1.394(3)
C(19)-C(20)	1.381(3)
C(20)-C(18)#1	1.394(3)
C(21)-C(22)	1.460(3)
C(23)-C(24)	1.468(4)
S(31A)-O(33A)	1.411(3)
S(31A)-O(31A)	1.437(6)
S(31A)-O(32A)	1.437(4)
S(31A)-C(31A)	1.776(7)
F(31A)-C(31A)	1.296(7)
F(32A)-C(31A)	1.324(7)
F(33A)-C(31A)	1.446(10)
S(31B)-O(33B)	1.410(9)
S(31B)-O(32B)	1.410(5)
S(31B)-O(31B)	1.414(5)
S(31B)-C(31B)	1.748(8)
F(31B)-C(31B)	1.314(8)
F(32B)-C(31B)	1.455(12)
F(33B)-C(31B)	1.295(13)
N(41)-C(42)	1.137(9)
C(42)-C(43)	1.443(9)

N(4)-Cu(1)-N(2)	119.54(8)
N(4)-Cu(1)-N(1)	125.66(8)
N(2)-Cu(1)-N(1)	90.79(8)
N(4)-Cu(1)-N(3)	117.95(8)
N(2)-Cu(1)-N(3)	101.75(8)
N(1)-Cu(1)-N(3)	95.11(8)
C(5)-N(1)-C(1)	117.6(2)
C(5)-N(1)-Cu(1)	120.54(15)
C(1)-N(1)-Cu(1)	120.62(17)
C(11)-N(2)-C(7)	118.2(2)
C(11)-N(2)-Cu(1)	119.67(16)
C(7)-N(2)-Cu(1)	121.68(16)
C(21)-N(3)-Cu(1)	154.5(2)
C(23)-N(4)-Cu(1)	172.1(2)
N(1)-C(1)-C(2)	123.3(2)
C(1)-C(2)-C(3)	118.6(2)
C(2)-C(3)-C(4)	119.5(3)
C(5)-C(4)-C(3)	118.8(3)
N(1)-C(5)-C(4)	122.2(2)
N(1)-C(5)-C(6)	116.7(2)
C(4)-C(5)-C(6)	121.1(2)
O(1)-C(6)-C(7)	106.21(19)
O(1)-C(6)-C(12)	109.73(17)
C(7)-C(6)-C(12)	112.77(18)
O(1)-C(6)-C(5)	109.34(18)
C(7)-C(6)-C(5)	107.69(17)
C(12)-C(6)-C(5)	110.9(2)
N(2)-C(7)-C(8)	121.6(2)
N(2)-C(7)-C(6)	116.6(2)
C(8)-C(7)-C(6)	121.8(2)
C(9)-C(8)-C(7)	119.2(2)
C(10)-C(9)-C(8)	119.3(2)
C(11)-C(10)-C(9)	118.2(2)
N(2)-C(11)-C(10)	123.5(2)
C(13)-C(12)-C(17)	117.9(2)
C(13)-C(12)-C(6)	120.2(2)
C(17)-C(12)-C(6)	121.7(2)
C(14)-C(13)-C(12)	122.6(2)
C(13)-C(14)-C(15)	119.0(2)
C(16)-C(15)-C(14)	119.5(2)
C(15)-C(16)-C(17)	122.2(2)
C(16)-C(17)-C(12)	118.5(2)
C(16)-C(17)-C(18)	117.3(2)
C(12)-C(17)-C(18)	124.1(2)
C(19)-C(18)-C(20)#1	118.3(2)
C(19)-C(18)-C(17)	121.4(2)
C(20)#1-C(18)-C(17)	120.2(2)
C(20)-C(19)-C(18)	121.0(2)
C(19)-C(20)-C(18)#1	120.7(2)
N(3)-C(21)-C(22)	179.3(3)
N(4)-C(23)-C(24)	179.7(3)
O(33A)-S(31A)-O(31A)	118.6(3)
O(33A)-S(31A)-O(32A)	114.6(2)
O(31A)-S(31A)-O(32A)	114.8(3)
O(33A)-S(31A)-C(31A)	104.3(3)
O(31A)-S(31A)-C(31A)	96.9(4)
O(32A)-S(31A)-C(31A)	103.8(3)
F(31A)-C(31A)-F(32A)	108.9(5)
F(31A)-C(31A)-F(33A)	105.3(6)
F(32A)-C(31A)-F(33A)	106.1(6)
F(31A)-C(31A)-S(31A)	114.6(5)
F(32A)-C(31A)-S(31A)	112.3(5)
F(33A)-C(31A)-S(31A)	109.1(5)
O(33B)-S(31B)-O(32B)	117.7(5)
O(33B)-S(31B)-O(31B)	113.9(6)
O(32B)-S(31B)-O(31B)	115.5(3)
O(33B)-S(31B)-C(31B)	98.4(6)
O(32B)-S(31B)-C(31B)	103.3(5)

O(31B)-S(31B)-C(31B)	104.8(4)	F(31B)-C(31B)-F(32B)	104.0(10)
F(33B)-C(31B)-F(31B)	112.2(7)	F(33B)-C(31B)-S(31B)	116.0(9)
F(33B)-C(31B)-F(32B)	102.8(8)	F(31B)-C(31B)-S(31B)	113.4(6)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Table A5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **[*p*-H_2LCu(I)$_2$](2OTf)** (CCDC 731671). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	233(2)	379(2)	260(2)	-92(2)	-44(1)	-98(1)
O(1)	207(9)	374(11)	764(15)	-365(11)	-128(10)	-18(8)
N(1)	158(10)	443(14)	270(12)	-202(11)	-63(9)	54(10)
N(2)	223(10)	201(11)	211(11)	-101(10)	-56(9)	12(8)
N(3)	348(13)	454(15)	415(15)	-55(12)	-197(12)	-132(11)
N(4)	282(12)	444(15)	287(13)	-17(12)	-96(11)	-152(11)
C(1)	212(13)	527(19)	240(15)	-179(15)	-64(12)	99(13)
C(2)	285(15)	540(20)	386(18)	-233(17)	-118(14)	225(15)
C(3)	490(18)	414(19)	540(20)	-317(17)	-211(17)	223(15)
C(4)	308(14)	397(18)	503(19)	-277(16)	-159(14)	94(13)
C(5)	213(12)	352(16)	337(16)	-231(14)	-104(12)	75(11)
C(6)	156(11)	284(15)	378(16)	-219(13)	-31(11)	-7(10)
C(7)	161(11)	137(13)	300(15)	-78(11)	-38(11)	34(10)
C(8)	200(12)	170(14)	409(17)	-43(13)	3(12)	27(10)
C(9)	302(14)	217(15)	286(17)	53(13)	91(12)	92(12)
C(10)	448(17)	284(16)	203(15)	-78(13)	-51(13)	122(14)
C(11)	316(14)	218(14)	264(15)	-97(12)	-85(12)	43(11)
C(12)	145(11)	357(15)	240(14)	-182(13)	-63(11)	11(11)
C(13)	161(12)	600(20)	325(16)	-306(16)	-84(12)	90(12)
C(14)	174(13)	820(20)	191(15)	-219(16)	-20(11)	-12(14)
C(15)	223(13)	531(19)	208(15)	-61(14)	-56(12)	-35(13)
C(16)	182(12)	363(16)	219(14)	-95(13)	-34(11)	0(11)
C(17)	126(11)	316(15)	192(13)	-115(12)	-36(10)	-21(10)
C(18)	141(10)	175(13)	160(12)	-40(11)	-39(10)	29(9)
C(19)	137(10)	196(13)	197(13)	-56(11)	-40(10)	-2(9)
C(20)	192(11)	201(13)	206(13)	-103(11)	-58(10)	17(10)
C(21)	289(14)	455(18)	261(15)	-144(14)	-19(12)	-188(13)
C(22)	222(14)	560(20)	860(30)	-392(19)	-147(16)	40(14)
C(23)	430(17)	550(20)	440(20)	-20(17)	-205(16)	-234(16)
C(24)	1210(30)	470(20)	860(30)	230(20)	-710(30)	-350(20)
S(31A)	300(7)	302(8)	262(8)	-90(7)	-78(6)	-50(6)
F(31A)	440(20)	450(20)	950(30)	-70(20)	-480(20)	27(18)
F(32A)	670(20)	410(20)	1220(40)	-270(20)	-400(30)	-214(18)
F(33A)	360(30)	1100(40)	750(40)	-540(30)	320(30)	-340(20)
O(31A)	690(40)	490(30)	260(30)	-140(20)	-90(30)	10(30)

O(32A)	500(20)	340(20)	370(30)	-150(20)	-250(20)	70(20)
O(33A)	410(20)	420(20)	420(30)	-220(20)	-140(20)	-92(18)
C(31A)	420(40)	620(50)	540(50)	-210(40)	-120(40)	-170(40)
S(31B)	518(12)	398(10)	218(9)	-92(8)	-56(9)	-181(8)
F(31B)	780(30)	1250(50)	290(30)	-150(30)	-230(30)	500(30)
F(32B)	510(40)	2870(120)	730(60)	380(70)	60(40)	-540(60)
F(33B)	2440(100)	2180(90)	890(50)	-1230(60)	-940(70)	1560(80)
O(31B)	1290(60)	620(40)	380(40)	-100(30)	-270(40)	270(40)
O(32B)	1510(60)	440(30)	690(40)	-80(30)	-680(40)	-310(30)
O(33B)	970(60)	1020(60)	1140(90)	-510(60)	-10(60)	-610(50)
C(31B)	450(50)	1720(110)	280(40)	-260(60)	-120(40)	390(60)
N(41)	670(40)	780(40)	390(30)	-220(30)	-110(30)	-90(30)
C(42)	470(40)	310(40)	390(50)	-120(40)	-160(40)	50(40)
C(43)	460(40)	430(50)	450(60)	-50(50)	-180(40)	-110(50)

Table A6. Crystal data and structure refinement for **[*m*-H_2LCu(II)$_2$](4OTf)** (CCDC 812331).

Empirical formula	$[C_{48}H_{42}N_8O_2Cu_2]^{+4}$ $4[CF_3O_3S]^{-}$ • $4(C_2H_3N)$	
Formula weight	1650.47	
Crystallization Solvent	Acetonitrile/diethyl ether	
Crystal Habit	Needle	
Crystal size	0.23 x 0.08 x 0.04 mm^3	
Crystal color	Blue	
	Data Collection	
Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKa	
Data Collection Temperature	100(2) K	
q range for 9958 reflections used in lattice determination	2.19 to 22.19°	
Unit cell dimensions	a = 10.1012(6) Å	a= 90°
	b = 24.0267(13) Å	b= 96.847(3)°
	c = 29.4602(16) Å	g = 90°
Volume	7099.0(7) Å^3	
Z	4	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Density (calculated)	1.544 Mg/m^3	
F(000)	3360	
Data collection program	Bruker APEX2 v2009.7-0	
q range for data collection	1.83 to 26.40°	
Completeness to q = 26.40°	99.4 %	
Index ranges	$-12 \le h \le 12$, $-29 \le k \le 29$, $-36 \le l \le 36$	
Data collection scan type	ω scans; 9 settings	
Data reduction program	Bruker SAINT-Plus v7.66A	
Reflections collected	109425	

Independent reflections	14497 [R_{int}= 0.0988]
Absorption coefficient	0.818 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9680 and 0.8341
	Structure solution and Refinement
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	14497 / 0 / 947
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.097
Final R indices [I>2s(I), 8438 reflections]	R1 = 0.0455, *w*R2 = 0.0479
R indices (all data)	R1 = 0.0984, *w*R2 = 0.0517
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Largest diff. peak and hole	0.761 and -0.732 e.Å^{-3}

Special Refinement Details for [*m*-H_2LCu(II)$_2$](4OTf). Crystals were mounted on in a loop using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

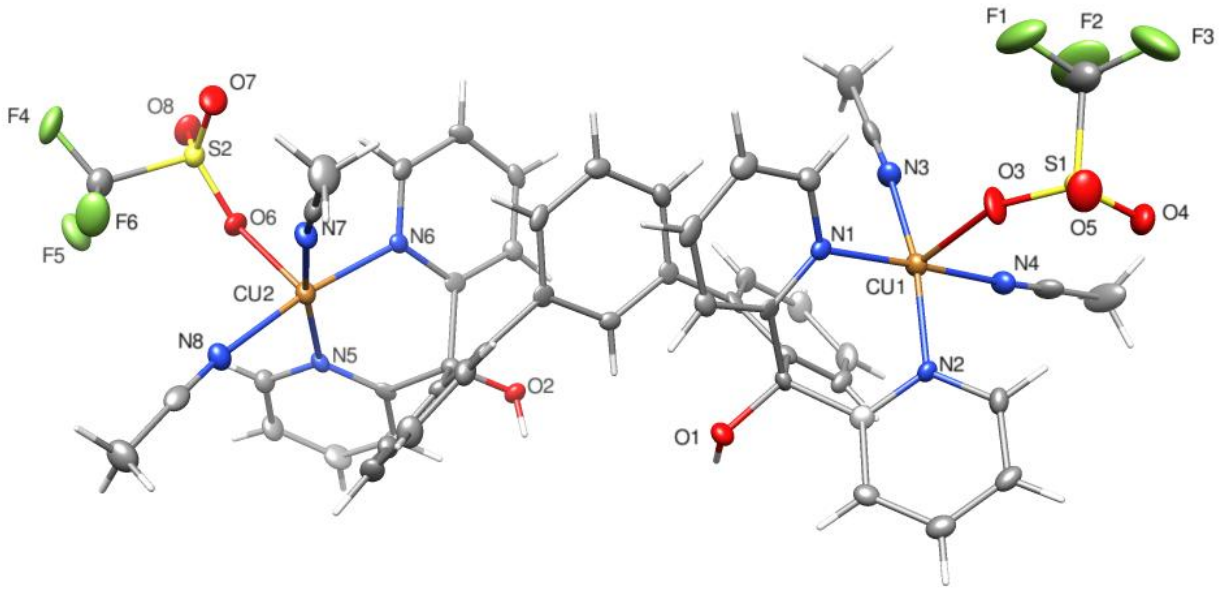


Figure A23. Structural drawing of **[*m*-H_2LCu(II)$_2$](4OTf)** with 50% thermal probability ellipsoids.

Table A7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **[*m*-H_2LCu(II)$_2$](4OTf)** (CCDC 812331). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cu(1)	5940(1)	5992(1)	6147(1)	17(1)
Cu(2)	14206(1)	5882(1)	8842(1)	17(1)
O(1)	7520(2)	6921(1)	7409(1)	17(1)
O(2)	12553(2)	6999(1)	7706(1)	16(1)
N(1)	6515(2)	5686(1)	6769(1)	13(1)
N(2)	5031(2)	6598(1)	6444(1)	13(1)
N(3)	7208(2)	5495(1)	5881(1)	21(1)
N(4)	5478(2)	6330(1)	5525(1)	21(1)
N(5)	14997(2)	6590(1)	8654(1)	14(1)
N(6)	13765(2)	5702(1)	8184(1)	13(1)
N(7)	13038(2)	5274(1)	9009(1)	19(1)
N(8)	14395(2)	6136(1)	9490(1)	20(1)
C(1)	6441(3)	5139(1)	6846(1)	16(1)
C(2)	6713(3)	4913(1)	7275(1)	20(1)
C(3)	7039(3)	5269(1)	7643(1)	19(1)
C(4)	7105(3)	5833(1)	7566(1)	15(1)
C(5)	6881(3)	6030(1)	7123(1)	12(1)
C(6)	7077(3)	6639(1)	6998(1)	13(1)
C(7)	5677(3)	6855(1)	6815(1)	14(1)
C(8)	5084(3)	7283(1)	7030(1)	16(1)
C(9)	3804(3)	7450(1)	6864(1)	20(1)

C(10)	3154(3)	7186(1)	6488(1)	19(1)
C(11)	3792(3)	6763(1)	6284(1)	17(1)
C(12)	8041(3)	5287(1)	5723(1)	22(1)
C(13)	9112(3)	5020(1)	5513(1)	33(1)
C(14)	5269(3)	6499(1)	5170(1)	26(1)
C(15)	5020(3)	6729(1)	4707(1)	50(1)
C(16)	8048(3)	6685(1)	6637(1)	13(1)
C(17)	7780(3)	7034(1)	6263(1)	18(1)
C(18)	8605(3)	7062(1)	5920(1)	23(1)
C(19)	9729(3)	6734(1)	5950(1)	23(1)
C(20)	10037(3)	6391(1)	6321(1)	19(1)
C(21)	9246(3)	6367(1)	6673(1)	14(1)
C(22)	9710(3)	6016(1)	7080(1)	13(1)
C(23)	9803(3)	5437(1)	7045(1)	16(1)
C(24)	10202(3)	5120(1)	7429(1)	16(1)
C(25)	10539(3)	5374(1)	7845(1)	16(1)
C(26)	10526(3)	5951(1)	7886(1)	13(1)
C(27)	10086(3)	6261(1)	7500(1)	12(1)
C(28)	10870(3)	6236(1)	8334(1)	14(1)
C(29)	10022(3)	6166(1)	8669(1)	18(1)
C(30)	10202(3)	6453(1)	9081(1)	22(1)
C(31)	11247(3)	6824(1)	9160(1)	23(1)
C(32)	12128(3)	6889(1)	8838(1)	17(1)
C(33)	11983(3)	6596(1)	8428(1)	14(1)
C(34)	13016(3)	6666(1)	8084(1)	14(1)
C(35)	14339(3)	6903(1)	8326(1)	13(1)
C(36)	14816(3)	7411(1)	8205(1)	16(1)
C(37)	16017(3)	7598(1)	8426(1)	24(1)
C(38)	16712(3)	7273(1)	8759(1)	22(1)
C(39)	16165(3)	6774(1)	8868(1)	19(1)
C(40)	13352(3)	6100(1)	7880(1)	13(1)
C(41)	13203(3)	6000(1)	7416(1)	14(1)
C(42)	13409(3)	5470(1)	7263(1)	16(1)
C(43)	13778(3)	5050(1)	7577(1)	17(1)
C(44)	13961(3)	5186(1)	8033(1)	16(1)
C(45)	12218(3)	4989(1)	9095(1)	20(1)
C(46)	11151(3)	4621(1)	9208(1)	33(1)
C(47)	14320(3)	6302(1)	9842(1)	20(1)
C(48)	14163(3)	6529(1)	10293(1)	31(1)
S(1)	2875(1)	5277(1)	5843(1)	20(1)
F(1)	3767(2)	4264(1)	5911(1)	68(1)
F(2)	4017(2)	4666(1)	5276(1)	80(1)
F(3)	2093(2)	4376(1)	5398(1)	75(1)
O(3)	4178(2)	5440(1)	6063(1)	31(1)
O(4)	2351(2)	5618(1)	5464(1)	30(1)
O(5)	1958(2)	5136(1)	6160(1)	35(1)
C(49)	3220(4)	4618(2)	5592(1)	44(1)

S(2)	16862(1)	4953(1)	8983(1)	21(1)
F(4)	18068(2)	4538(1)	9746(1)	41(1)
F(5)	18284(2)	5423(1)	9674(1)	46(1)
F(6)	16430(2)	5079(1)	9835(1)	49(1)
O(6)	16194(2)	5484(1)	8888(1)	21(1)
O(7)	15989(2)	4478(1)	8943(1)	34(1)
O(8)	18077(2)	4899(1)	8779(1)	29(1)
C(50)	17429(3)	4999(1)	9586(1)	29(1)
S(3)	4970(1)	3204(1)	7370(1)	30(1)
F(7)	6568(2)	3454(1)	6770(1)	76(1)
F(8)	4512(2)	3406(1)	6501(1)	119(1)
F(9)	5613(2)	2654(1)	6667(1)	78(1)
O(9)	5030(2)	3781(1)	7486(1)	43(1)
O(10)	3637(2)	2980(1)	7307(1)	53(1)
O(11)	5942(2)	2864(1)	7628(1)	60(1)
C(51)	5440(4)	3186(2)	6803(2)	55(1)
S(4)	7055(1)	2003(1)	4770(1)	30(1)
F(10)	5430(2)	1775(1)	4030(1)	70(1)
F(11)	4760(2)	1479(1)	4641(1)	42(1)
F(12)	4646(2)	2341(1)	4485(1)	97(1)
O(12)	7685(2)	1479(1)	4716(1)	77(1)
O(13)	6800(2)	2124(1)	5223(1)	40(1)
O(14)	7594(3)	2454(1)	4538(1)	90(1)
C(52)	5382(4)	1900(2)	4472(1)	35(1)
N(9)	-733(3)	4105(1)	6338(1)	56(1)
C(53)	298(4)	4036(2)	6534(1)	42(1)
C(54)	1612(3)	3957(1)	6781(1)	55(1)
N(10)	1945(3)	4068(1)	8238(1)	62(1)
C(55)	2837(4)	3788(2)	8368(1)	43(1)
C(56)	3974(3)	3436(1)	8536(1)	52(1)
N(11)	11366(3)	2820(1)	5305(1)	64(1)
C(57)	10384(4)	3042(2)	5316(1)	43(1)
C(58)	9104(3)	3316(1)	5322(1)	45(1)
N(12)	9412(3)	3520(1)	7449(1)	49(1)
C(59)	8906(4)	3647(1)	7757(1)	39(1)
C(60)	8248(4)	3790(2)	8153(1)	62(1)

Table A8. Selected bond lengths [Å] and angles [°] for **[*m*-H_2LCu(II)$_2$](4OTf)** (CCDC 812331).

Cu(1)-N(3)	1.980(3)	N(3)-Cu(1)-N(2)	167.00(10)
Cu(1)-N(2)	1.981(2)	N(3)-Cu(1)-N(1)	90.61(10)
Cu(1)-N(1)	1.994(2)	N(2)-Cu(1)-N(1)	87.96(10)
Cu(1)-N(4)	2.008(3)	N(3)-Cu(1)-N(4)	88.47(10)
Cu(1)-O(3)	2.2086(19)	N(2)-Cu(1)-N(4)	92.08(10)
Cu(2)-N(7)	1.976(2)	N(1)-Cu(1)-N(4)	176.05(10)
Cu(2)-N(6)	1.984(2)	N(3)-Cu(1)-O(3)	98.31(9)
Cu(2)-N(5)	1.986(2)	N(2)-Cu(1)-O(3)	94.64(9)
Cu(2)-N(8)	1.992(2)	N(1)-Cu(1)-O(3)	91.40(9)
Cu(2)-O(6)	2.2133(19)	N(4)-Cu(1)-O(3)	92.54(9)
		N(7)-Cu(2)-N(6)	90.69(10)
		N(7)-Cu(2)-N(5)	167.02(10)
		N(6)-Cu(2)-N(5)	88.03(10)
		N(7)-Cu(2)-N(8)	88.81(10)
		N(6)-Cu(2)-N(8)	171.06(10)
		N(5)-Cu(2)-N(8)	90.45(10)
		N(7)-Cu(2)-O(6)	103.31(9)
		N(6)-Cu(2)-O(6)	93.63(8)
		N(5)-Cu(2)-O(6)	89.66(8)
		N(8)-Cu(2)-O(6)	95.17(9)

Table A9. Bond lengths [Å] and angles [°] for **[*m*-H_2LCu(II)$_2$](4OTf)** (CCDC 812331).

Cu(1)-N(3)	1.980(3)	N(7)-C(45)	1.126(3)
Cu(1)-N(2)	1.981(2)	N(8)-C(47)	1.122(3)
Cu(1)-N(1)	1.994(2)	C(1)-C(2)	1.374(4)
Cu(1)-N(4)	2.008(3)	C(2)-C(3)	1.390(4)
Cu(1)-O(3)	2.2086(19)	C(3)-C(4)	1.376(4)
Cu(2)-N(7)	1.976(2)	C(4)-C(5)	1.382(4)
Cu(2)-N(6)	1.984(2)	C(5)-C(6)	1.526(4)
Cu(2)-N(5)	1.986(2)	C(6)-C(16)	1.534(4)
Cu(2)-N(8)	1.992(2)	C(6)-C(7)	1.543(4)
Cu(2)-O(6)	2.2133(19)	C(7)-C(8)	1.381(4)
O(1)-C(6)	1.413(3)	C(8)-C(9)	1.386(4)
O(2)-C(34)	1.405(3)	C(9)-C(10)	1.375(4)
N(1)-C(1)	1.339(3)	C(10)-C(11)	1.377(4)
N(1)-C(5)	1.349(3)	C(12)-C(13)	1.457(4)
N(2)-C(11)	1.343(3)	C(14)-C(15)	1.465(4)
N(2)-C(7)	1.352(3)	C(16)-C(17)	1.384(4)
N(3)-C(12)	1.126(3)	C(16)-C(21)	1.425(4)
N(4)-C(14)	1.119(4)	C(17)-C(18)	1.386(4)
N(5)-C(35)	1.339(3)	C(18)-C(19)	1.377(4)
N(5)-C(39)	1.344(3)	C(19)-C(20)	1.376(4)
N(6)-C(44)	1.338(3)	C(20)-C(21)	1.384(4)
N(6)-C(40)	1.342(3)	C(21)-C(22)	1.492(4)

C(22)-C(27)	1.382(4)	S(4)-O(12)	1.428(2)
C(22)-C(23)	1.401(4)	S(4)-C(52)	1.827(4)
C(23)-C(24)	1.383(4)	F(10)-C(52)	1.341(4)
C(24)-C(25)	1.375(4)	F(11)-C(52)	1.319(4)
C(25)-C(26)	1.392(4)	F(12)-C(52)	1.298(4)
C(26)-C(27)	1.388(4)	N(9)-C(53)	1.141(4)
C(26)-C(28)	1.490(4)	C(53)-C(54)	1.448(4)
C(28)-C(29)	1.392(4)	N(10)-C(55)	1.152(4)
C(28)-C(33)	1.418(4)	C(55)-C(56)	1.464(4)
C(29)-C(30)	1.388(4)	N(11)-C(57)	1.131(4)
C(30)-C(31)	1.380(4)	C(57)-C(58)	1.452(4)
C(31)-C(32)	1.383(3)	N(12)-C(59)	1.134(4)
C(32)-C(33)	1.391(4)	C(59)-C(60)	1.452(4)
C(33)-C(34)	1.549(4)		
C(34)-C(40)	1.540(4)	N(3)-Cu(1)-N(2)	167.00(10)
C(34)-C(35)	1.547(4)	N(3)-Cu(1)-N(1)	90.61(10)
C(35)-C(36)	1.374(4)	N(2)-Cu(1)-N(1)	87.96(10)
C(36)-C(37)	1.382(4)	N(3)-Cu(1)-N(4)	88.47(10)
C(37)-C(38)	1.379(4)	N(2)-Cu(1)-N(4)	92.08(10)
C(38)-C(39)	1.374(4)	N(1)-Cu(1)-N(4)	176.05(10)
C(40)-C(41)	1.377(4)	N(3)-Cu(1)-O(3)	98.31(9)
C(41)-C(42)	1.376(4)	N(2)-Cu(1)-O(3)	94.64(9)
C(42)-C(43)	1.389(4)	N(1)-Cu(1)-O(3)	91.40(9)
C(43)-C(44)	1.374(4)	N(4)-Cu(1)-O(3)	92.54(9)
C(45)-C(46)	1.464(4)	N(7)-Cu(2)-N(6)	90.69(10)
C(47)-C(48)	1.462(4)	N(7)-Cu(2)-N(5)	167.02(10)
S(1)-O(5)	1.432(2)	N(6)-Cu(2)-N(5)	88.03(10)
S(1)-O(4)	1.433(2)	N(7)-Cu(2)-N(8)	88.81(10)
S(1)-O(3)	1.4505(19)	N(6)-Cu(2)-N(8)	171.06(10)
S(1)-C(49)	1.799(4)	N(5)-Cu(2)-N(8)	90.45(10)
F(1)-C(49)	1.337(4)	N(7)-Cu(2)-O(6)	103.31(9)
F(2)-C(49)	1.307(4)	N(6)-Cu(2)-O(6)	93.63(8)
F(3)-C(49)	1.343(4)	N(5)-Cu(2)-O(6)	89.66(8)
S(2)-O(8)	1.4361(19)	N(8)-Cu(2)-O(6)	95.17(9)
S(2)-O(7)	1.440(2)	C(1)-N(1)-C(5)	119.1(3)
S(2)-O(6)	1.4550(19)	C(1)-N(1)-Cu(1)	120.1(2)
S(2)-C(50)	1.803(3)	C(5)-N(1)-Cu(1)	120.6(2)
F(4)-C(50)	1.339(3)	C(11)-N(2)-C(7)	119.2(3)
F(5)-C(50)	1.340(3)	C(11)-N(2)-Cu(1)	121.5(2)
F(6)-C(50)	1.331(3)	C(7)-N(2)-Cu(1)	119.3(2)
S(3)-O(9)	1.4262(19)	C(12)-N(3)-Cu(1)	169.1(3)
S(3)-O(11)	1.426(2)	C(14)-N(4)-Cu(1)	176.2(3)
S(3)-O(10)	1.442(2)	C(35)-N(5)-C(39)	119.0(3)
S(3)-C(51)	1.791(4)	C(35)-N(5)-Cu(2)	120.1(2)
F(7)-C(51)	1.323(4)	C(39)-N(5)-Cu(2)	120.8(2)
F(8)-C(51)	1.324(4)	C(44)-N(6)-C(40)	119.0(3)
F(9)-C(51)	1.357(4)	C(44)-N(6)-Cu(2)	120.0(2)
S(4)-O(13)	1.419(2)	C(40)-N(6)-Cu(2)	120.8(2)
S(4)-O(14)	1.422(2)	C(45)-N(7)-Cu(2)	169.1(3)

C(47)-N(8)-Cu(2)	170.3(3)	C(31)-C(32)-C(33)	121.8(3)
N(1)-C(1)-C(2)	122.4(3)	C(32)-C(33)-C(28)	118.5(3)
C(1)-C(2)-C(3)	118.5(3)	C(32)-C(33)-C(34)	120.3(3)
C(4)-C(3)-C(2)	119.3(3)	C(28)-C(33)-C(34)	121.3(3)
C(3)-C(4)-C(5)	119.2(3)	O(2)-C(34)-C(40)	105.2(2)
N(1)-C(5)-C(4)	121.3(3)	O(2)-C(34)-C(35)	110.0(2)
N(1)-C(5)-C(6)	115.5(3)	C(40)-C(34)-C(35)	106.7(2)
C(4)-C(5)-C(6)	123.1(3)	O(2)-C(34)-C(33)	113.2(2)
O(1)-C(6)-C(5)	106.8(2)	C(40)-C(34)-C(33)	110.9(2)
O(1)-C(6)-C(16)	113.4(2)	C(35)-C(34)-C(33)	110.6(2)
C(5)-C(6)-C(16)	110.4(2)	N(5)-C(35)-C(36)	121.8(3)
O(1)-C(6)-C(7)	108.8(2)	N(5)-C(35)-C(34)	116.9(3)
C(5)-C(6)-C(7)	105.5(2)	C(36)-C(35)-C(34)	121.3(3)
C(16)-C(6)-C(7)	111.6(2)	C(35)-C(36)-C(37)	118.8(3)
N(2)-C(7)-C(8)	121.1(3)	C(38)-C(37)-C(36)	119.7(3)
N(2)-C(7)-C(6)	117.5(3)	C(39)-C(38)-C(37)	118.4(3)
C(8)-C(7)-C(6)	121.3(3)	N(5)-C(39)-C(38)	122.3(3)
C(7)-C(8)-C(9)	119.4(3)	N(6)-C(40)-C(41)	121.7(3)
C(10)-C(9)-C(8)	119.0(3)	N(6)-C(40)-C(34)	115.8(3)
C(9)-C(10)-C(11)	119.2(3)	C(41)-C(40)-C(34)	122.5(3)
N(2)-C(11)-C(10)	122.0(3)	C(42)-C(41)-C(40)	119.0(3)
N(3)-C(12)-C(13)	179.2(4)	C(41)-C(42)-C(43)	119.5(3)
N(4)-C(14)-C(15)	178.7(4)	C(44)-C(43)-C(42)	118.2(3)
C(17)-C(16)-C(21)	117.9(3)	N(6)-C(44)-C(43)	122.5(3)
C(17)-C(16)-C(6)	121.0(3)	N(7)-C(45)-C(46)	179.8(4)
C(21)-C(16)-C(6)	121.1(3)	N(8)-C(47)-C(48)	177.4(4)
C(16)-C(17)-C(18)	122.2(3)	O(5)-S(1)-O(4)	115.83(13)
C(19)-C(18)-C(17)	119.3(3)	O(5)-S(1)-O(3)	113.30(14)
C(20)-C(19)-C(18)	120.0(3)	O(4)-S(1)-O(3)	115.19(13)
C(19)-C(20)-C(21)	121.7(3)	O(5)-S(1)-C(49)	103.34(16)
C(20)-C(21)-C(16)	118.8(3)	O(4)-S(1)-C(49)	104.67(16)
C(20)-C(21)-C(22)	118.1(3)	O(3)-S(1)-C(49)	102.25(16)
C(16)-C(21)-C(22)	123.1(3)	S(1)-O(3)-Cu(1)	152.64(14)
C(27)-C(22)-C(23)	118.4(3)	F(2)-C(49)-F(1)	108.5(3)
C(27)-C(22)-C(21)	120.3(3)	F(2)-C(49)-F(3)	107.4(3)
C(23)-C(22)-C(21)	121.3(3)	F(1)-C(49)-F(3)	106.3(3)
C(24)-C(23)-C(22)	120.2(3)	F(2)-C(49)-S(1)	112.4(3)
C(25)-C(24)-C(23)	120.1(3)	F(1)-C(49)-S(1)	110.8(3)
C(24)-C(25)-C(26)	121.1(3)	F(3)-C(49)-S(1)	111.1(3)
C(27)-C(26)-C(25)	117.9(3)	O(8)-S(2)-O(7)	116.08(13)
C(27)-C(26)-C(28)	119.8(3)	O(8)-S(2)-O(6)	113.44(12)
C(25)-C(26)-C(28)	122.1(3)	O(7)-S(2)-O(6)	114.55(13)
C(22)-C(27)-C(26)	122.2(3)	O(8)-S(2)-C(50)	103.33(14)
C(29)-C(28)-C(33)	118.4(3)	O(7)-S(2)-C(50)	104.45(15)
C(29)-C(28)-C(26)	118.3(3)	O(6)-S(2)-C(50)	102.81(14)
C(33)-C(28)-C(26)	123.2(3)	S(2)-O(6)-Cu(2)	141.84(12)
C(30)-C(29)-C(28)	122.1(3)	F(6)-C(50)-F(4)	107.0(3)
C(31)-C(30)-C(29)	119.1(3)	F(6)-C(50)-F(5)	107.2(3)
C(30)-C(31)-C(32)	120.0(3)	F(4)-C(50)-F(5)	106.7(3)

F(6)-C(50)-S(2)	112.3(2)	O(13)-S(4)-O(12)	114.76(17)
F(4)-C(50)-S(2)	112.3(2)	O(14)-S(4)-O(12)	114.60(18)
F(5)-C(50)-S(2)	111.0(2)	O(13)-S(4)-C(52)	102.64(15)
O(9)-S(3)-O(11)	114.97(16)	O(14)-S(4)-C(52)	104.91(17)
O(9)-S(3)-O(10)	114.03(14)	O(12)-S(4)-C(52)	103.01(16)
O(11)-S(3)-O(10)	115.32(16)	F(12)-C(52)-F(11)	108.3(3)
O(9)-S(3)-C(51)	103.88(19)	F(12)-C(52)-F(10)	107.4(3)
O(11)-S(3)-C(51)	103.92(17)	F(11)-C(52)-F(10)	105.7(3)
O(10)-S(3)-C(51)	102.50(18)	F(12)-C(52)-S(4)	112.0(2)
F(7)-C(51)-F(8)	107.6(4)	F(11)-C(52)-S(4)	112.1(2)
F(7)-C(51)-F(9)	107.1(3)	F(10)-C(52)-S(4)	111.0(3)
F(8)-C(51)-F(9)	106.6(4)	N(9)-C(53)-C(54)	179.2(5)
F(7)-C(51)-S(3)	112.5(3)	N(10)-C(55)-C(56)	179.5(5)
F(8)-C(51)-S(3)	111.8(3)	N(11)-C(57)-C(58)	178.4(5)
F(9)-C(51)-S(3)	110.9(3)	N(12)-C(59)-C(60)	177.9(4)
O(13)-S(4)-O(14)	114.76(16)		

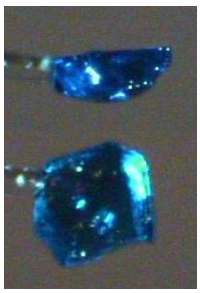
Table A10. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **[*m*-H_2LCu(II)$_2$](4OTf)** (CCDC 812331). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	184(2)	189(2)	144(2)	-7(2)	16(2)	13(2)
Cu(2)	197(2)	175(2)	140(2)	8(2)	0(2)	-19(2)
O(1)	184(14)	163(14)	170(12)	-16(10)	9(10)	-36(10)
O(2)	159(14)	167(13)	168(12)	7(10)	31(10)	51(10)
N(1)	90(15)	136(15)	174(15)	18(13)	19(12)	-2(12)
N(2)	101(16)	144(15)	144(15)	15(12)	19(13)	22(12)
N(3)	207(18)	247(17)	176(16)	-31(13)	24(14)	27(14)
N(4)	270(18)	199(17)	154(16)	-8(14)	9(14)	27(13)
N(5)	163(16)	153(15)	101(15)	-19(12)	14(13)	-32(12)
N(6)	92(15)	144(15)	140(15)	-13(12)	13(12)	-14(12)
N(7)	202(18)	200(17)	168(16)	19(13)	3(13)	-66(13)
N(8)	204(17)	252(18)	155(16)	-4(14)	28(14)	-25(13)
C(1)	132(19)	170(20)	193(19)	-7(16)	21(15)	-29(15)
C(2)	130(20)	200(20)	290(20)	44(17)	47(17)	-25(15)
C(3)	80(19)	280(20)	220(20)	89(17)	35(16)	27(16)
C(4)	100(18)	200(20)	154(18)	-19(16)	31(15)	-16(15)
C(5)	30(17)	161(19)	181(18)	-6(16)	26(14)	31(14)
C(6)	127(19)	164(19)	97(17)	-29(15)	-9(15)	7(15)
C(7)	150(20)	154(19)	128(18)	51(15)	82(15)	-32(15)
C(8)	180(20)	130(18)	164(18)	2(15)	58(16)	-32(15)
C(9)	230(20)	160(20)	220(20)	33(16)	80(17)	33(16)
C(10)	170(20)	170(20)	240(20)	68(16)	49(16)	44(16)
C(11)	140(20)	210(20)	157(18)	29(16)	-16(15)	-13(16)

C(12)	210(20)	260(20)	151(19)	-31(16)	-53(16)	-61(17)
C(13)	200(20)	520(30)	260(20)	-75(19)	50(17)	85(19)
C(14)	360(20)	200(20)	220(20)	-65(18)	62(19)	80(18)
C(15)	920(30)	400(30)	190(20)	50(20)	70(20)	290(20)
C(16)	125(19)	125(18)	130(18)	-25(14)	15(15)	-42(15)
C(17)	116(19)	165(19)	260(20)	24(16)	5(16)	9(15)
C(18)	260(20)	250(20)	171(19)	97(16)	-7(17)	-56(17)
C(19)	160(20)	370(20)	190(20)	51(17)	82(17)	-51(17)
C(20)	94(19)	270(20)	200(20)	-20(16)	25(16)	30(16)
C(21)	131(19)	157(19)	118(18)	-33(15)	-10(15)	-85(15)
C(22)	44(17)	200(20)	156(18)	-4(15)	44(14)	-14(15)
C(23)	106(19)	220(20)	151(18)	-37(16)	-2(15)	3(15)
C(24)	115(19)	145(19)	240(20)	-3(16)	58(16)	-17(15)
C(25)	78(18)	200(20)	192(19)	75(16)	2(15)	-4(15)
C(26)	38(17)	184(19)	181(18)	-4(16)	40(14)	7(15)
C(27)	87(17)	124(17)	170(17)	-13(16)	47(14)	-3(15)
C(28)	150(20)	128(18)	150(18)	40(15)	-13(16)	80(15)
C(29)	150(20)	190(20)	197(19)	32(16)	-12(16)	-8(15)
C(30)	180(20)	330(20)	180(20)	30(17)	66(16)	9(17)
C(31)	260(20)	270(20)	147(19)	-53(16)	33(17)	121(18)
C(32)	160(20)	164(19)	174(19)	-4(15)	-10(16)	-5(15)
C(33)	137(19)	127(18)	145(18)	11(15)	37(15)	31(15)
C(34)	180(20)	116(18)	127(18)	1(14)	6(15)	16(15)
C(35)	106(19)	167(19)	126(18)	-60(15)	67(15)	-9(15)
C(36)	180(20)	159(19)	156(18)	18(15)	33(16)	14(15)
C(37)	250(20)	210(20)	270(20)	-19(17)	67(17)	-122(17)
C(38)	200(20)	250(20)	220(20)	-7(17)	-24(16)	-73(17)
C(39)	170(20)	230(20)	176(19)	-14(16)	1(16)	8(16)
C(40)	43(18)	153(19)	196(19)	-11(15)	34(15)	-34(14)
C(41)	106(18)	175(19)	152(18)	0(15)	33(15)	-21(15)
C(42)	96(19)	260(20)	132(18)	-45(16)	7(15)	-16(16)
C(43)	109(19)	183(19)	227(19)	-74(16)	52(16)	8(15)
C(44)	102(19)	160(19)	199(19)	25(15)	-12(15)	-9(15)
C(45)	250(20)	200(20)	149(19)	38(16)	-35(17)	51(17)
C(46)	250(20)	390(20)	350(20)	81(19)	10(18)	-135(19)
C(47)	180(20)	140(20)	260(20)	61(17)	15(18)	-50(15)
C(48)	410(20)	340(20)	190(20)	-19(18)	96(18)	-40(19)
S(1)	209(5)	192(5)	195(5)	-28(4)	-20(4)	0(4)
F(1)	1110(20)	401(15)	502(16)	10(12)	-41(15)	397(14)
F(2)	1090(20)	910(20)	441(16)	-123(15)	326(16)	508(17)
F(3)	1180(20)	358(15)	621(18)	-172(13)	-282(16)	-120(14)
O(3)	212(14)	340(15)	343(15)	51(12)	-104(12)	-140(11)
O(4)	306(15)	275(14)	281(14)	28(12)	-98(12)	38(11)
O(5)	253(15)	499(17)	302(15)	18(13)	98(12)	-4(12)
C(49)	600(30)	360(30)	320(20)	-60(20)	-80(20)	140(20)
S(2)	236(5)	198(5)	175(5)	12(4)	-8(4)	9(4)
F(4)	440(14)	452(14)	317(13)	162(11)	-81(10)	128(11)

F(5)	545(15)	483(15)	307(13)	-57(11)	-93(11)	-150(12)
F(6)	507(15)	722(16)	259(12)	74(12)	170(11)	167(12)
O(6)	173(13)	204(13)	244(13)	-1(11)	-15(11)	50(10)
O(7)	381(16)	226(14)	371(16)	49(12)	-85(12)	-129(12)
O(8)	233(15)	397(16)	251(14)	27(12)	78(12)	110(12)
C(50)	280(20)	320(20)	260(20)	29(19)	12(19)	30(20)
S(3)	378(6)	164(5)	368(6)	9(4)	97(5)	2(5)
F(7)	511(17)	679(18)	1170(20)	144(16)	486(17)	43(14)
F(8)	720(20)	2280(40)	580(19)	580(20)	171(16)	730(20)
F(9)	640(18)	1010(20)	699(19)	-381(17)	158(15)	28(16)
O(9)	305(14)	126(13)	850(20)	-107(15)	58(13)	-4(12)
O(10)	529(18)	321(16)	790(20)	-152(15)	269(16)	-305(14)
O(11)	960(20)	389(17)	439(19)	57(14)	-19(16)	458(16)
C(51)	330(30)	610(30)	710(40)	170(30)	60(30)	190(30)
S(4)	356(6)	320(6)	220(5)	-4(5)	13(5)	-81(5)
F(10)	1000(20)	787(18)	276(14)	-12(13)	-145(13)	-493(15)
F(11)	316(13)	482(15)	472(15)	72(12)	50(11)	-89(11)
F(12)	872(19)	386(16)	1410(30)	-354(16)	-819(17)	403(14)
O(12)	295(17)	670(20)	1330(30)	-610(20)	18(18)	62(15)
O(13)	312(15)	719(19)	171(14)	-92(13)	13(12)	4(13)
O(14)	1300(30)	960(20)	349(18)	323(17)	-283(18)	-910(20)
C(52)	510(30)	250(20)	270(20)	-7(19)	-80(20)	-10(20)
N(9)	770(30)	480(20)	450(20)	-60(20)	80(20)	-200(20)
C(53)	600(30)	290(20)	430(30)	-30(20)	250(20)	-100(30)
C(54)	550(30)	390(30)	770(30)	70(20)	330(30)	60(20)
N(10)	800(30)	370(20)	700(30)	10(20)	60(20)	-110(20)
C(55)	630(40)	320(30)	340(30)	-30(20)	60(30)	-250(20)
C(56)	580(30)	500(30)	430(30)	110(20)	-160(20)	-210(20)
N(11)	770(30)	700(30)	440(20)	150(20)	60(20)	300(20)
C(57)	740(40)	310(30)	250(20)	20(20)	30(20)	100(20)
C(58)	650(30)	360(30)	350(30)	-110(20)	30(20)	20(20)
N(12)	630(30)	340(20)	510(20)	0(19)	60(20)	-22(18)
C(59)	570(30)	150(20)	440(30)	30(20)	-40(20)	80(20)
C(60)	770(30)	700(30)	360(30)	-260(20)	-150(20)	420(30)

Table A11. Crystal data and structure refinement for **[HLCu(II)](2OTf)** (CCDC 812332).



Empirical formula	$[C_{27}H_{24}N_4O_4Cu]^{+2}\ 2[CF_3O_3S]^{-}$	
Formula weight	782.18	
Crystallization Solvent	Acetonitrile/diethyl ether	
Crystal Habit	Plate	
Crystal size	0.31 x 0.28 x 0.07 mm^3	
Crystal color	Blue	
	Data Collection	
Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKa	
Data Collection Temperature	100(2) K	
q range for 9772 reflections used in lattice determination	2.39 to 33.10°	
Unit cell dimensions	a = 14.6607(6) Å	a= 90°
	b = 10.6262(4) Å	b= 104.507(2)°
	c = 21.5889(9) Å	g = 90°
Volume	3256.0(2) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	P $2_1/c$	
Density (calculated)	1.596 Mg/m^3	
F(000)	1588	
Data collection program	Bruker APEX2 v2009.7-0	
q range for data collection	1.95 to 33.26°	
Completeness to q = 33.26°	99.8 %	
Index ranges	$-22 \le h \le 22$, $-16 \le k \le 16$, $-33 \le l \le 33$	
Data collection scan type	ω scans; 12 settings	
Data reduction program	Bruker SAINT-Plus v7.66A	
Reflections collected	114858	
Independent reflections	12515 [R_{int}= 0.0482]	
Absorption coefficient	0.885 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.9406 and 0.7709	
	Structure solution and Refinement	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Geometric positions	
Structure refinement program	SHELXL-97 (Sheldrick, 2008)	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	12515 / 0 / 445	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	2.343	
Final R indices [I>2s(I), 9700 reflections]	R1 = 0.0380, *w*R2 = 0.0577	
R indices (all data)	R1 = 0.0523, *w*R2 = 0.0583	
Type of weighting scheme used	Sigma	
Weighting scheme used	$w=1/\sigma^2(Fo^2)$	

Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	1.019 and -0.951 e.Å^{-3}

Special Refinement Details for [HLCu(II)](2OTf). Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

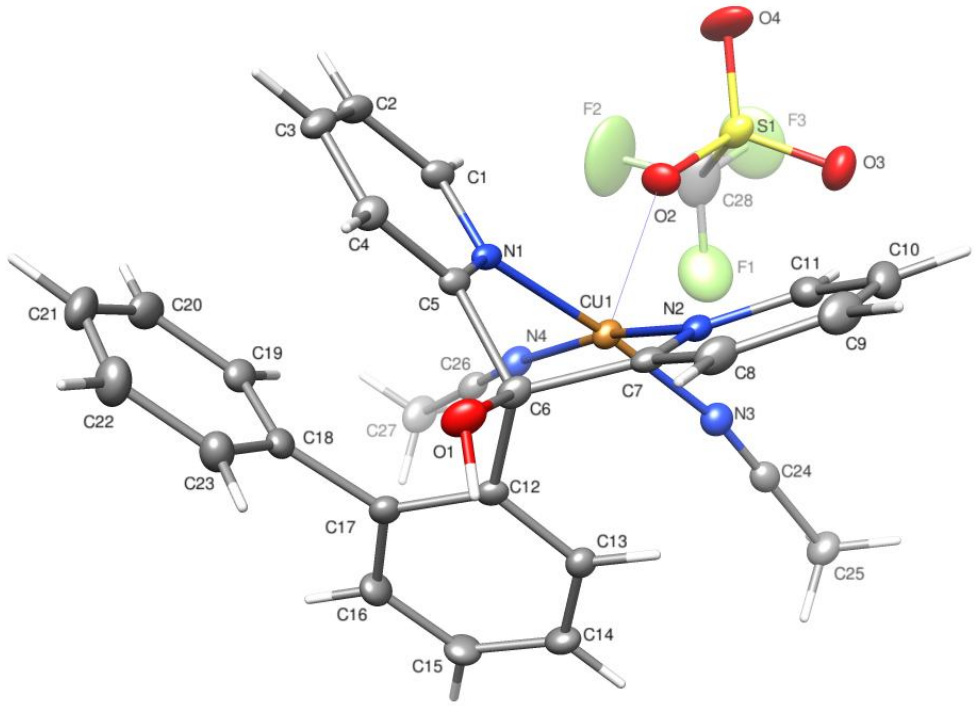


Figure A24. Structural drawing of **[HLCu(II)](2OTf)** with 50% thermal probability ellipsoids.

Table A12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **[HLCu(II)](2OTf)** (CCDC 812332). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cu(1)	2959(1)	7275(1)	3957(1)	14(1)
S(1)	4924(1)	8653(1)	3541(1)	21(1)
F(1)	3717(1)	10503(1)	3486(1)	56(1)

F(2)	4872(1)	10505(1)	4322(1)	79(1)
F(3)	5090(1)	11082(1)	3418(1)	78(1)
O(1)	2159(1)	3442(1)	4477(1)	19(1)
O(2)	4398(1)	7937(1)	3908(1)	22(1)
O(3)	4585(1)	8534(1)	2864(1)	33(1)
O(4)	5927(1)	8583(1)	3786(1)	41(1)
N(1)	3556(1)	6269(1)	4732(1)	13(1)
N(2)	2960(1)	5696(1)	3458(1)	14(1)
N(3)	2242(1)	8180(1)	3181(1)	18(1)
N(4)	2737(1)	8710(1)	4490(1)	19(1)
C(1)	4297(1)	6743(1)	5169(1)	16(1)
C(2)	4777(1)	6048(1)	5688(1)	18(1)
C(3)	4511(1)	4817(1)	5749(1)	18(1)
C(4)	3752(1)	4319(1)	5297(1)	16(1)
C(5)	3272(1)	5086(1)	4805(1)	13(1)
C(6)	2381(1)	4668(1)	4308(1)	14(1)
C(7)	2659(1)	4615(1)	3668(1)	14(1)
C(8)	2667(1)	3500(1)	3337(1)	19(1)
C(9)	3001(1)	3498(2)	2796(1)	24(1)
C(10)	3318(1)	4604(2)	2582(1)	23(1)
C(11)	3275(1)	5692(1)	2925(1)	19(1)
C(12)	1571(1)	5605(1)	4306(1)	13(1)
C(13)	1002(1)	6037(1)	3729(1)	15(1)
C(14)	295(1)	6920(1)	3714(1)	19(1)
C(15)	152(1)	7363(1)	4277(1)	22(1)
C(16)	684(1)	6913(1)	4857(1)	21(1)
C(17)	1395(1)	6027(1)	4883(1)	16(1)
C(18)	1931(1)	5598(1)	5532(1)	19(1)
C(19)	2504(1)	6445(2)	5947(1)	20(1)
C(20)	3032(1)	6059(2)	6543(1)	26(1)
C(21)	2981(1)	4827(2)	6735(1)	31(1)
C(22)	2382(1)	3989(2)	6339(1)	31(1)
C(23)	1856(1)	4368(2)	5741(1)	24(1)
C(24)	1728(1)	8708(1)	2787(1)	16(1)
C(25)	1060(1)	9384(1)	2285(1)	21(1)
C(26)	2520(1)	9538(1)	4751(1)	17(1)
C(27)	2249(1)	10595(1)	5096(1)	25(1)
C(28)	4635(2)	10270(2)	3700(1)	43(1)
F(4)	1456(1)	6482(1)	1668(1)	70(1)
F(5)	656(1)	5391(1)	887(1)	78(1)
F(6)	840(1)	4715(1)	1846(1)	63(1)
O(5)	-156(1)	6909(1)	2197(1)	41(1)
O(6)	-393(1)	7608(1)	1101(1)	26(1)
O(7)	-1092(1)	5644(1)	1341(1)	36(1)
S(2)	-360(1)	6561(1)	1538(1)	19(1)
C(29)	700(1)	5744(2)	1478(1)	40(1)

Table A13. Selected bond lengths [Å] and angles [°] for **[HLCu(II)](2OTf)** (CCDC 812332).

Cu(1)-N(4)	1.9859(13)	N(4)-Cu(1)-N(3)	89.35(5)
Cu(1)-N(3)	1.9885(12)	N(4)-Cu(1)-N(1)	91.55(5)
Cu(1)-N(1)	1.9932(11)	N(3)-Cu(1)-N(1)	174.10(5)
Cu(1)-N(2)	1.9954(11)	N(4)-Cu(1)-N(2)	169.04(5)
Cu(1)-O(2)	2.2522(9)	N(3)-Cu(1)-N(2)	91.32(5)
		N(1)-Cu(1)-N(2)	86.70(5)
		N(4)-Cu(1)-O(2)	94.52(4)
		N(3)-Cu(1)-O(2)	96.48(4)
		N(1)-Cu(1)-O(2)	89.27(4)
		N(2)-Cu(1)-O(2)	96.28(4)

Table A14. Bond lengths [Å] and angles [°] for **[HLCu(II)](2OTf)** (CCDC 812332).

Cu(1)-N(4)	1.9859(13)	C(12)-C(17)	1.4078(19)
Cu(1)-N(3)	1.9885(12)	C(13)-C(14)	1.3935(18)
Cu(1)-N(1)	1.9932(11)	C(14)-C(15)	1.367(2)
Cu(1)-N(2)	1.9954(11)	C(15)-C(16)	1.383(2)
Cu(1)-O(2)	2.2522(9)	C(16)-C(17)	1.3956(19)
S(1)-O(3)	1.4267(11)	C(17)-C(18)	1.4948(19)
S(1)-O(4)	1.4343(10)	C(18)-C(19)	1.394(2)
S(1)-O(2)	1.4506(10)	C(18)-C(23)	1.396(2)
S(1)-C(28)	1.8225(19)	C(19)-C(20)	1.386(2)
F(1)-C(28)	1.332(2)	C(20)-C(21)	1.381(2)
F(2)-C(28)	1.323(2)	C(21)-C(22)	1.386(2)
F(3)-C(28)	1.329(2)	C(22)-C(23)	1.388(2)
O(1)-C(6)	1.4119(16)	C(24)-C(25)	1.4540(19)
N(1)-C(5)	1.3453(17)	C(26)-C(27)	1.457(2)
N(1)-C(1)	1.3462(16)	F(4)-C(29)	1.336(2)
N(2)-C(11)	1.3412(18)	F(5)-C(29)	1.316(2)
N(2)-C(7)	1.3495(17)	F(6)-C(29)	1.337(2)
N(3)-C(24)	1.1340(17)	O(5)-S(2)	1.4266(12)
N(4)-C(26)	1.1313(17)	O(6)-S(2)	1.4512(10)
C(1)-C(2)	1.3798(19)	O(7)-S(2)	1.4331(11)
C(2)-C(3)	1.3798(19)	S(2)-C(29)	1.8128(18)
C(3)-C(4)	1.3883(18)		
C(4)-C(5)	1.3833(18)	N(4)-Cu(1)-N(3)	89.35(5)
C(5)-C(6)	1.5330(18)	N(4)-Cu(1)-N(1)	91.55(5)
C(6)-C(7)	1.5360(19)	N(3)-Cu(1)-N(1)	174.10(5)
C(6)-C(12)	1.5491(18)	N(4)-Cu(1)-N(2)	169.04(5)
C(7)-C(8)	1.3857(19)	N(3)-Cu(1)-N(2)	91.32(5)
C(8)-C(9)	1.375(2)	N(1)-Cu(1)-N(2)	86.70(5)
C(9)-C(10)	1.385(2)	N(4)-Cu(1)-O(2)	94.52(4)
C(10)-C(11)	1.383(2)	N(3)-Cu(1)-O(2)	96.48(4)
C(12)-C(13)	1.3925(18)	N(1)-Cu(1)-O(2)	89.27(4)

N(2)-Cu(1)-O(2)	96.28(4)	C(13)-C(12)-C(6)	120.12(13)
O(3)-S(1)-O(4)	115.74(8)	C(17)-C(12)-C(6)	120.83(12)
O(3)-S(1)-O(2)	114.60(7)	C(12)-C(13)-C(14)	121.18(14)
O(4)-S(1)-O(2)	114.07(7)	C(15)-C(14)-C(13)	119.39(14)
O(3)-S(1)-C(28)	103.83(8)	C(14)-C(15)-C(16)	120.53(14)
O(4)-S(1)-C(28)	104.15(9)	C(15)-C(16)-C(17)	121.08(14)
O(2)-S(1)-C(28)	102.18(8)	C(16)-C(17)-C(12)	118.66(13)
S(1)-O(2)-Cu(1)	145.25(6)	C(16)-C(17)-C(18)	117.13(13)
C(5)-N(1)-C(1)	119.13(12)	C(12)-C(17)-C(18)	124.20(12)
C(5)-N(1)-Cu(1)	121.05(9)	C(19)-C(18)-C(23)	118.68(14)
C(1)-N(1)-Cu(1)	119.67(10)	C(19)-C(18)-C(17)	119.77(14)
C(11)-N(2)-C(7)	119.89(13)	C(23)-C(18)-C(17)	121.54(13)
C(11)-N(2)-Cu(1)	120.83(10)	C(20)-C(19)-C(18)	120.81(15)
C(7)-N(2)-Cu(1)	119.26(10)	C(21)-C(20)-C(19)	119.99(15)
C(24)-N(3)-Cu(1)	169.48(12)	C(20)-C(21)-C(22)	119.83(15)
C(26)-N(4)-Cu(1)	172.75(12)	C(21)-C(22)-C(23)	120.38(16)
N(1)-C(1)-C(2)	121.83(13)	C(22)-C(23)-C(18)	120.19(15)
C(3)-C(2)-C(1)	119.03(13)	N(3)-C(24)-C(25)	179.36(16)
C(2)-C(3)-C(4)	119.39(13)	N(4)-C(26)-C(27)	179.00(16)
C(5)-C(4)-C(3)	118.63(14)	F(2)-C(28)-F(3)	107.89(16)
N(1)-C(5)-C(4)	121.83(12)	F(2)-C(28)-F(1)	107.69(19)
N(1)-C(5)-C(6)	115.05(12)	F(3)-C(28)-F(1)	107.40(16)
C(4)-C(5)-C(6)	123.12(12)	F(2)-C(28)-S(1)	110.80(14)
O(1)-C(6)-C(5)	107.35(11)	F(3)-C(28)-S(1)	111.05(15)
O(1)-C(6)-C(7)	109.23(11)	F(1)-C(28)-S(1)	111.85(12)
C(5)-C(6)-C(7)	105.59(11)	O(5)-S(2)-O(7)	115.20(7)
O(1)-C(6)-C(12)	111.52(11)	O(5)-S(2)-O(6)	114.42(7)
C(5)-C(6)-C(12)	109.49(11)	O(7)-S(2)-O(6)	115.35(6)
C(7)-C(6)-C(12)	113.33(11)	O(5)-S(2)-C(29)	103.06(9)
N(2)-C(7)-C(8)	120.52(14)	O(7)-S(2)-C(29)	104.17(8)
N(2)-C(7)-C(6)	117.07(12)	O(6)-S(2)-C(29)	102.18(8)
C(8)-C(7)-C(6)	122.26(13)	F(5)-C(29)-F(4)	107.49(17)
C(9)-C(8)-C(7)	119.39(15)	F(5)-C(29)-F(6)	107.79(16)
C(8)-C(9)-C(10)	120.12(14)	F(4)-C(29)-F(6)	107.80(16)
C(11)-C(10)-C(9)	117.89(15)	F(5)-C(29)-S(2)	111.80(14)
N(2)-C(11)-C(10)	122.17(15)	F(4)-C(29)-S(2)	110.91(13)
C(13)-C(12)-C(17)	119.05(12)	F(6)-C(29)-S(2)	110.87(13)

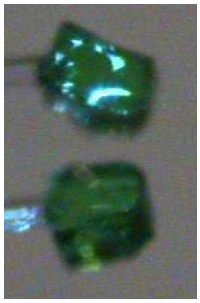
Table A15. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **[HLCu(II)](2OTf)** (CCDC 812332). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	154(1)	120(1)	139(1)	-4(1)	12(1)	16(1)
S(1)	196(2)	205(2)	191(2)	40(2)	5(2)	-49(2)
F(1)	755(8)	272(6)	674(9)	73(6)	240(7)	191(6)
F(2)	1359(12)	458(8)	481(8)	-281(7)	112(9)	-254(8)

F(3)	1105(10)	264(7)	1058(12)	127(7)	437(10)	-255(7)
O(1)	179(5)	130(5)	223(6)	22(4)	-13(4)	-44(4)
O(2)	186(5)	189(6)	273(6)	63(5)	61(5)	-28(4)
O(3)	374(7)	411(8)	183(6)	10(5)	27(5)	16(6)
O(4)	170(5)	558(9)	446(8)	171(7)	-17(6)	-113(6)
N(1)	109(5)	140(6)	134(6)	-23(5)	16(5)	14(5)
N(2)	109(5)	156(6)	130(6)	-9(5)	6(5)	25(5)
N(3)	200(6)	152(6)	186(7)	-9(5)	39(5)	8(5)
N(4)	206(6)	154(7)	178(7)	8(5)	8(5)	25(5)
C(1)	131(6)	162(7)	173(7)	-43(6)	28(6)	-15(6)
C(2)	123(7)	231(8)	164(8)	-43(6)	-5(6)	2(6)
C(3)	151(7)	217(8)	155(7)	7(6)	0(6)	60(6)
C(4)	171(7)	138(7)	168(7)	7(6)	25(6)	22(6)
C(5)	110(6)	133(7)	133(7)	-27(5)	21(5)	5(5)
C(6)	149(7)	104(7)	153(7)	2(6)	-3(6)	-17(5)
C(7)	93(6)	156(7)	145(7)	-11(6)	-9(5)	19(5)
C(8)	187(7)	156(8)	203(8)	-42(6)	-13(6)	1(6)
C(9)	234(8)	226(9)	225(8)	-99(7)	4(7)	55(7)
C(10)	201(7)	316(10)	163(8)	-49(7)	40(6)	71(7)
C(11)	141(7)	245(8)	165(8)	4(6)	24(6)	18(6)
C(12)	99(6)	136(7)	152(7)	-4(6)	12(5)	-27(5)
C(13)	142(7)	176(7)	137(7)	-18(6)	22(6)	-23(6)
C(14)	129(7)	230(8)	196(8)	34(6)	5(6)	6(6)
C(15)	150(7)	253(9)	248(8)	6(7)	55(6)	55(6)
C(16)	179(7)	294(9)	179(8)	-33(7)	70(6)	14(6)
C(17)	123(6)	208(8)	149(7)	-2(6)	18(6)	-31(6)
C(18)	141(7)	297(9)	134(7)	9(6)	55(6)	13(6)
C(19)	182(7)	271(9)	162(8)	-14(7)	53(6)	22(7)
C(20)	220(8)	400(11)	160(8)	-45(7)	31(7)	-10(7)
C(21)	276(9)	478(12)	155(8)	80(8)	31(7)	47(8)
C(22)	331(9)	368(10)	221(9)	103(8)	68(8)	-28(8)
C(23)	224(8)	329(10)	176(8)	31(7)	53(7)	-48(7)
C(24)	176(7)	136(7)	173(7)	-29(6)	51(6)	-17(6)
C(25)	226(7)	194(8)	188(8)	20(6)	6(6)	32(6)
C(26)	170(7)	159(8)	162(7)	31(6)	-3(6)	-12(6)
C(27)	310(8)	194(8)	229(9)	-41(7)	24(7)	55(7)
C(28)	657(14)	226(10)	394(12)	-6(9)	111(11)	-155(10)
F(4)	195(5)	421(7)	1448(14)	317(8)	130(7)	17(5)
F(5)	1286(12)	306(7)	1090(12)	-77(7)	922(11)	69(7)
F(6)	426(6)	283(6)	1174(12)	346(7)	173(7)	121(5)
O(5)	730(9)	305(7)	208(7)	-36(5)	157(7)	-173(6)
O(6)	201(5)	297(7)	292(6)	154(5)	54(5)	32(5)
O(7)	275(6)	454(8)	282(7)	108(6)	-50(5)	-203(6)
S(2)	183(2)	212(2)	173(2)	44(2)	18(2)	-9(2)
C(29)	330(10)	186(9)	731(16)	92(10)	203(11)	35(8)

Table A16. Crystal data and structure refinement for **[*p*-LCu(II)$_2$]$_2$(4OTf)**.

Empirical formula	$[C_{88}H_{68}N_{12}O_4Cu_4]^{+4}\ 4(CF_3O_3S)^{-} \bullet 2(C_2H_3N)$
Formula weight	2290.09
Crystallization Solvent	Acetonitrile
Crystal Habit	Block
Crystal size	0.24 x 0.19 x 0.16 mm^3
Crystal color	Green



Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKa	
Data Collection Temperature	100(2) K	
q range for 9692 reflections used in lattice determination	2.39 to 28.25°	
Unit cell dimensions	a = 26.9462(10) Å	a= 90°
	b = 15.2290(5) Å	b= 97.104(2)°
	c = 23.7114(8) Å	g = 90°
Volume	9655.6(6) Å^3	
Z	4	
Crystal system	Monoclinic	
Space group	C 2/*c*	
Density (calculated)	1.575 Mg/m^3	
F(000)	4656	
q range for data collection	1.52 to 28.51°	
Completeness to q = 28.51°	99.7 %	
Index ranges	$-36 \le h \le 33$, $-20 \le k \le 20$, $-31 \le l \le 31$	
Data collection scan type	ω scans; 14 settings	
Reflections collected	115303	
Independent reflections	12209 [R_{int}= 0.0471]	
Absorption coefficient	1.053 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.8496 and 0.7862	

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	12209 / 105 / 732
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	3.475
Final R indices [I>2s(I), 9191 reflections]	R1 = 0.0512, *w*R2 = 0.0756
R indices (all data)	R1 = 0.0756, *w*R2 = 0.0765
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$

Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	1.138 and -0.892 e.Å^{-3}

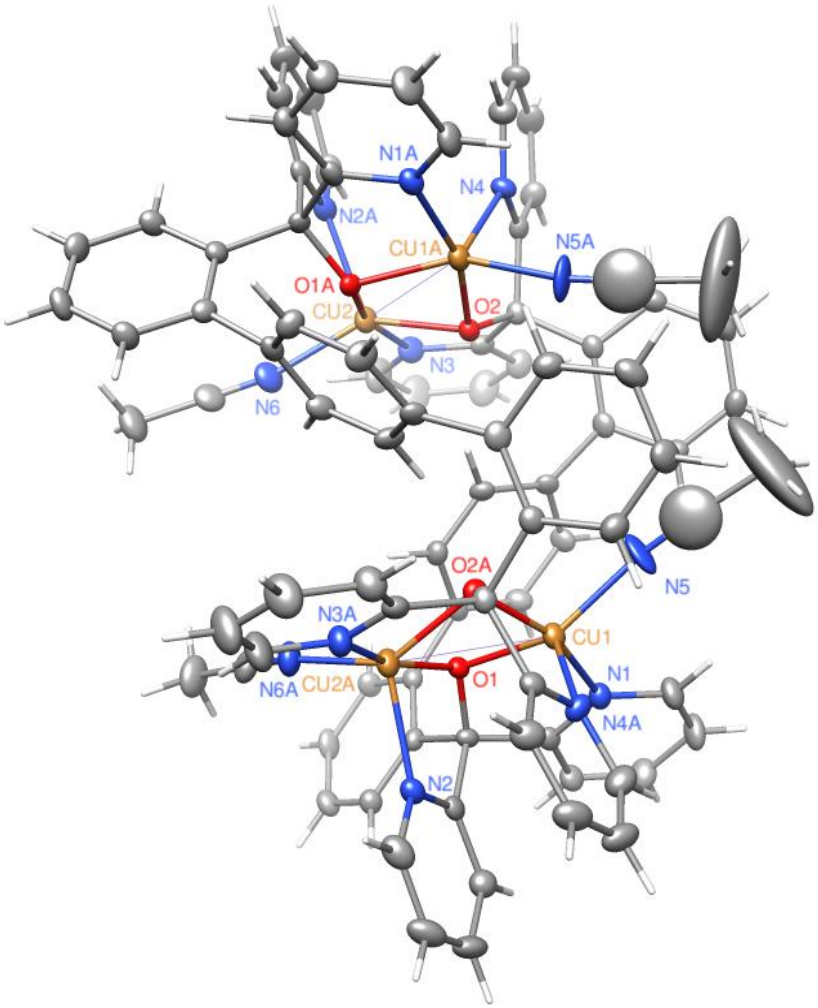


Figure A25. Structural drawing of **[*p*-LCu(II)$_2$]$_2$(4OTf)** with 50% thermal probability ellipsoids.

Special Refinement Details for [*p*-LCu(II)$_2$]$_2$(4OTf). Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. One of the triflate anions is disordered. Both orientations were restrained to be similar in geometry to the non-disordered triflate. Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table A17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **[*p*-LCu(II)$_2$]$_2$(4OTf)** (CCDC 812330). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Cu(1)	11097(1)	3515(1)	1993(1)	20(1)	1
Cu(2)	8711(1)	1894(1)	2393(1)	22(1)	1
O(1)	11058(1)	2248(1)	1843(1)	17(1)	1
O(2)	8939(1)	3095(1)	2244(1)	18(1)	1
N(1)	11175(1)	3535(1)	1177(1)	20(1)	1
N(2)	11957(1)	1775(1)	2206(1)	20(1)	1
N(3)	8505(1)	1920(2)	1570(1)	25(1)	1
N(4)	8184(1)	3918(1)	2564(1)	21(1)	1
N(5)	10745(1)	4668(2)	2045(1)	37(1)	1
N(6)	8972(1)	634(2)	2490(1)	30(1)	1
C(1)	11121(1)	4236(2)	831(1)	27(1)	1
C(2)	11154(1)	4171(2)	258(1)	32(1)	1
C(3)	11255(1)	3362(2)	37(1)	29(1)	1
C(4)	11314(1)	2645(2)	390(1)	23(1)	1
C(5)	11270(1)	2742(2)	963(1)	18(1)	1
C(6)	11325(1)	1992(2)	1399(1)	16(1)	1
C(7)	11879(1)	1891(2)	1643(1)	18(1)	1
C(8)	12271(1)	1938(2)	1320(1)	24(1)	1
C(9)	12757(1)	1862(2)	1584(1)	31(1)	1
C(10)	12837(1)	1746(2)	2161(1)	33(1)	1
C(11)	12428(1)	1701(2)	2458(1)	30(1)	1
C(12)	11104(1)	1146(2)	1116(1)	17(1)	1
C(13)	11405(1)	440(2)	1009(1)	21(1)	1
C(14)	11212(1)	-312(2)	738(1)	24(1)	1
C(15)	10706(1)	-367(2)	558(1)	24(1)	1
C(16)	10400(1)	327(2)	657(1)	22(1)	1
C(17)	10584(1)	1086(2)	933(1)	18(1)	1
C(18)	10224(1)	1810(2)	1019(1)	18(1)	1
C(19)	10047(1)	2366(2)	576(1)	22(1)	1
C(20)	9745(1)	3076(2)	667(1)	23(1)	1
C(21)	9606(1)	3251(2)	1202(1)	18(1)	1
C(22)	9766(1)	2668(2)	1638(1)	21(1)	1
C(23)	10061(1)	1954(2)	1544(1)	21(1)	1
C(24)	9350(1)	4105(2)	1293(1)	19(1)	1
C(25)	9589(1)	4850(2)	1111(1)	22(1)	1
C(26)	9409(1)	5684(2)	1165(1)	25(1)	1
C(27)	8974(1)	5796(2)	1400(1)	27(1)	1
C(28)	8725(1)	5077(2)	1577(1)	24(1)	1
C(29)	8902(1)	4227(2)	1539(1)	18(1)	1
C(30)	8620(1)	3464(2)	1780(1)	16(1)	1
C(31)	8135(1)	3750(2)	2007(1)	18(1)	1
C(32)	7679(1)	3817(2)	1673(1)	26(1)	1
C(33)	7261(1)	4042(2)	1927(1)	31(1)	1

C(34)	7311(1)	4220(2)	2495(1)	30(1)	1
C(35)	7777(1)	4157(2)	2798(1)	28(1)	1
C(36)	8498(1)	2732(2)	1347(1)	21(1)	1
C(37)	8368(1)	2868(2)	770(1)	28(1)	1
C(38)	8254(1)	2161(2)	421(1)	40(1)	1
C(39)	8273(1)	1330(2)	646(1)	44(1)	1
C(40)	8399(1)	1230(2)	1225(1)	38(1)	1
C(41)	10642(2)	5334(4)	2126(2)	96(2)	1
C(42)	10516(3)	6352(4)	2241(2)	206(4)	1
C(43)	9090(1)	-40(2)	2654(1)	29(1)	1
C(44)	9242(1)	-904(2)	2871(1)	41(1)	1
S(1)	8783(1)	8441(1)	1344(1)	43(1)	1
F(1)	9583(1)	8456(2)	825(1)	98(1)	1
F(2)	9570(1)	9436(1)	1462(1)	72(1)	1
F(3)	9116(1)	9576(2)	665(1)	83(1)	1
O(3)	9039(1)	7864(1)	1759(1)	80(1)	1
O(4)	8518(1)	9144(1)	1578(1)	43(1)	1
O(5)	8520(1)	8016(2)	857(1)	63(1)	1
C(52)	9284(1)	8983(2)	1060(1)	55(1)	1
S(2)	1581(1)	6582(2)	1070(1)	93(1)	0.593(2)
F(4)	843(2)	7572(3)	628(2)	150(4)	0.593(2)
F(5)	870(2)	7365(3)	1517(2)	211(4)	0.593(2)
F(6)	620(1)	6341(4)	939(3)	95(3)	0.593(2)
O(6)	1876(2)	7363(3)	1159(2)	186(6)	0.593(2)
O(7)	1599(2)	6165(2)	530(1)	81(2)	0.593(2)
O(8)	1611(2)	5993(3)	1546(2)	124(4)	0.593(2)
C(53)	958(2)	6987(3)	1028(2)	84(3)	0.593(2)
N(7)	2411(1)	4837(3)	-438(1)	82(1)	1
C(54)	2426(1)	4634(3)	15(2)	68(1)	1
C(56)	2443(1)	4430(3)	620(1)	68(1)	1
S(2B)	1620(1)	6889(2)	1244(1)	38(1)	0.407(2)
F(4B)	945(2)	7534(3)	471(2)	46(2)	0.407(2)
F(5B)	714(2)	6397(5)	889(2)	49(2)	0.407(2)
F(6B)	1219(1)	6276(2)	271(1)	39(1)	0.407(2)
O(6B)	1998(2)	7292(5)	957(2)	55(3)	0.407(2)
O(7B)	1724(3)	5999(2)	1421(2)	60(3)	0.407(2)
O(8B)	1420(2)	7433(3)	1656(2)	43(2)	0.407(2)
C(53B)	1107(1)	6787(3)	697(2)	30(2)	0.407(2)

Table A18. Selected bond lengths [Å] and angles [°] for **[*p*-LCu(II)$_2$]$_2$(4OTf)** (CCDC 812330).

Cu(1)-O(2)#1	1.9326(16)	O(2)#1-Cu(1)-O(1)	80.64(7)
Cu(1)-O(1)	1.9623(16)	O(2)#1-Cu(1)-N(1)	161.34(8)
Cu(1)-N(1)	1.973(2)	O(1)-Cu(1)-N(1)	81.17(8)
Cu(1)-N(5)	2.007(2)	O(2)#1-Cu(1)-N(5)	98.81(9)
Cu(1)-N(4)#1	2.173(2)	O(1)-Cu(1)-N(5)	148.76(9)
Cu(1)-Cu(2)#1	2.8787(4)	N(1)-Cu(1)-N(5)	98.87(10)
Cu(2)-O(1)#1	1.9186(16)	O(2)#1-Cu(1)-N(4)#1	77.71(7)
Cu(2)-N(3)	1.964(2)	O(1)-Cu(1)-N(4)#1	113.02(7)
Cu(2)-O(2)	1.9754(16)	N(1)-Cu(1)-N(4)#1	105.88(8)
Cu(2)-N(6)	2.047(2)	N(5)-Cu(1)-N(4)#1	97.13(10)
Cu(2)-N(2)#1	2.145(2)	O(2)#1-Cu(1)-Cu(2)#1	43.13(5)
Cu(2)-Cu(1)#1	2.8788(4)	O(1)-Cu(1)-Cu(2)#1	41.54(5)
		N(1)-Cu(1)-Cu(2)#1	118.35(6)
		N(5)-Cu(1)-Cu(2)#1	140.88(8)
		N(4)#1-Cu(1)-Cu(2)#1	84.56(6)
		O(1)#1-Cu(2)-N(3)	162.24(8)
		O(1)#1-Cu(2)-O(2)	80.65(7)
		N(3)-Cu(2)-O(2)	81.91(8)
		O(1)#1-Cu(2)-N(6)	95.22(8)
		N(3)-Cu(2)-N(6)	100.44(9)
		O(2)-Cu(2)-N(6)	141.11(8)
		O(1)#1-Cu(2)-N(2)#1	78.33(7)
		N(3)-Cu(2)-N(2)#1	106.98(8)
		O(2)-Cu(2)-N(2)#1	117.06(7)
		N(6)-Cu(2)-N(2)#1	99.54(9)
		O(1)#1-Cu(2)-Cu(1)#1	42.70(5)
		N(3)-Cu(2)-Cu(1)#1	119.76(7)
		O(2)-Cu(2)-Cu(1)#1	41.98(5)
		N(6)-Cu(2)-Cu(1)#1	135.22(6)
		N(2)#1-Cu(2)-Cu(1)#1	87.52(6)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+1/2

Table A19. Bond lengths [Å] and angles [°] for **[*p*-LCu(II)$_2$]$_2$(4OTf)** (CCDC 812330).

Cu(1)-O(2)#1	1.9326(16)	Cu(2)-N(6)	2.047(2)
Cu(1)-O(1)	1.9623(16)	Cu(2)-N(2)#1	2.145(2)
Cu(1)-N(1)	1.973(2)	Cu(2)-Cu(1)#1	2.8788(4)
Cu(1)-N(5)	2.007(2)	O(1)-C(6)	1.401(3)
Cu(1)-N(4)#1	2.173(2)	O(2)-C(30)	1.424(3)
Cu(1)-Cu(2)#1	2.8787(4)	N(1)-C(1)	1.342(3)
Cu(2)-O(1)#1	1.9186(16)	N(1)-C(5)	1.347(3)
Cu(2)-N(3)	1.964(2)	N(2)-C(7)	1.337(3)
Cu(2)-O(2)	1.9754(16)	N(2)-C(11)	1.341(3)

N(3)-C(40)	1.341(3)	C(43)-C(44)	1.453(4)
N(3)-C(36)	1.345(3)	S(1)-O(5)	1.4340(19)
N(4)-C(31)	1.335(3)	S(1)-O(4)	1.4351(18)
N(4)-C(35)	1.340(3)	S(1)-O(3)	1.433(2)
N(5)-C(41)	1.076(5)	S(1)-C(52)	1.783(3)
N(6)-C(43)	1.129(3)	F(1)-C(52)	1.309(3)
C(1)-C(2)	1.378(3)	F(2)-C(52)	1.342(3)
C(2)-C(3)	1.378(4)	F(3)-C(52)	1.339(3)
C(3)-C(4)	1.373(3)	S(2)-O(7)	1.436(2)
C(4)-C(5)	1.386(3)	S(2)-O(6)	1.431(2)
C(5)-C(6)	1.535(3)	S(2)-O(8)	1.436(2)
C(6)-C(12)	1.540(3)	S(2)-C(53)	1.782(3)
C(6)-C(7)	1.540(3)	F(4)-C(53)	1.309(3)
C(7)-C(8)	1.381(3)	F(5)-C(53)	1.341(3)
C(8)-C(9)	1.384(4)	F(6)-C(53)	1.339(3)
C(9)-C(10)	1.372(4)	N(7)-C(54)	1.114(4)
C(10)-C(11)	1.379(4)	C(54)-C(56)	1.462(5)
C(12)-C(13)	1.388(3)	S(2B)-O(6B)	1.431(2)
C(12)-C(17)	1.417(3)	S(2B)-O(7B)	1.436(2)
C(13)-C(14)	1.382(3)	S(2B)-O(8B)	1.435(2)
C(14)-C(15)	1.381(3)	S(2B)-C(53B)	1.782(3)
C(15)-C(16)	1.379(3)	F(4B)-C(53B)	1.309(3)
C(16)-C(17)	1.389(3)	F(5B)-C(53B)	1.342(3)
C(17)-C(18)	1.499(3)	F(6B)-C(53B)	1.340(3)
C(18)-C(19)	1.386(3)		
C(18)-C(23)	1.388(3)	O(2)#1-Cu(1)-O(1)	80.64(7)
C(19)-C(20)	1.386(3)	O(2)#1-Cu(1)-N(1)	161.34(8)
C(20)-C(21)	1.392(3)	O(1)-Cu(1)-N(1)	81.17(8)
C(21)-C(22)	1.392(3)	O(2)#1-Cu(1)-N(5)	98.81(9)
C(21)-C(24)	1.500(3)	O(1)-Cu(1)-N(5)	148.76(9)
C(22)-C(23)	1.382(3)	N(1)-Cu(1)-N(5)	98.87(10)
C(24)-C(25)	1.398(3)	O(2)#1-Cu(1)-N(4)#1	77.71(7)
C(24)-C(29)	1.418(3)	O(1)-Cu(1)-N(4)#1	113.02(7)
C(25)-C(26)	1.371(3)	N(1)-Cu(1)-N(4)#1	105.88(8)
C(26)-C(27)	1.370(3)	N(5)-Cu(1)-N(4)#1	97.13(10)
C(27)-C(28)	1.378(3)	O(2)#1-Cu(1)-Cu(2)#1	43.13(5)
C(28)-C(29)	1.386(3)	O(1)-Cu(1)-Cu(2)#1	41.54(5)
C(29)-C(30)	1.536(3)	N(1)-Cu(1)-Cu(2)#1	118.35(6)
C(30)-C(36)	1.523(3)	N(5)-Cu(1)-Cu(2)#1	140.88(8)
C(30)-C(31)	1.537(3)	N(4)#1-Cu(1)-Cu(2)#1	84.56(6)
C(31)-C(32)	1.382(3)	O(1)#1-Cu(2)-N(3)	162.24(8)
C(32)-C(33)	1.383(4)	O(1)#1-Cu(2)-O(2)	80.65(7)
C(33)-C(34)	1.365(4)	N(3)-Cu(2)-O(2)	81.91(8)
C(34)-C(35)	1.370(4)	O(1)#1-Cu(2)-N(6)	95.22(8)
C(36)-C(37)	1.385(3)	N(3)-Cu(2)-N(6)	100.44(9)
C(37)-C(38)	1.368(4)	O(2)-Cu(2)-N(6)	141.11(8)
C(38)-C(39)	1.372(4)	O(1)#1-Cu(2)-N(2)#1	78.33(7)
C(39)-C(40)	1.381(4)	N(3)-Cu(2)-N(2)#1	106.98(8)
C(41)-C(42)	1.617(7)	O(2)-Cu(2)-N(2)#1	117.06(7)

N(6)-Cu(2)-N(2)#1	99.54(9)	C(14)-C(13)-C(12)	122.1(2)
O(1)#1-Cu(2)-Cu(1)#1	42.70(5)	C(15)-C(14)-C(13)	119.7(2)
N(3)-Cu(2)-Cu(1)#1	119.76(7)	C(14)-C(15)-C(16)	119.2(2)
O(2)-Cu(2)-Cu(1)#1	41.98(5)	C(15)-C(16)-C(17)	122.2(2)
N(6)-Cu(2)-Cu(1)#1	135.22(6)	C(16)-C(17)-C(12)	118.6(2)
N(2)#1-Cu(2)-Cu(1)#1	87.52(6)	C(16)-C(17)-C(18)	118.4(2)
C(6)-O(1)-Cu(2)#1	119.55(14)	C(12)-C(17)-C(18)	123.0(2)
C(6)-O(1)-Cu(1)	112.87(14)	C(19)-C(18)-C(23)	117.7(2)
Cu(2)#1-O(1)-Cu(1)	95.76(7)	C(19)-C(18)-C(17)	121.0(2)
C(30)-O(2)-Cu(1)#1	119.75(14)	C(23)-C(18)-C(17)	121.2(2)
C(30)-O(2)-Cu(2)	109.40(13)	C(20)-C(19)-C(18)	120.9(2)
Cu(1)#1-O(2)-Cu(2)	94.88(7)	C(19)-C(20)-C(21)	121.3(2)
C(1)-N(1)-C(5)	119.7(2)	C(22)-C(21)-C(20)	117.5(2)
C(1)-N(1)-Cu(1)	126.46(18)	C(22)-C(21)-C(24)	123.5(2)
C(5)-N(1)-Cu(1)	113.77(17)	C(20)-C(21)-C(24)	118.5(2)
C(7)-N(2)-C(11)	118.6(2)	C(23)-C(22)-C(21)	120.9(2)
C(7)-N(2)-Cu(2)#1	113.24(16)	C(22)-C(23)-C(18)	121.4(2)
C(11)-N(2)-Cu(2)#1	127.68(18)	C(25)-C(24)-C(29)	118.0(2)
C(40)-N(3)-C(36)	119.4(2)	C(25)-C(24)-C(21)	115.0(2)
C(40)-N(3)-Cu(2)	127.1(2)	C(29)-C(24)-C(21)	127.1(2)
C(36)-N(3)-Cu(2)	113.41(17)	C(26)-C(25)-C(24)	122.8(3)
C(31)-N(4)-C(35)	118.4(2)	C(27)-C(26)-C(25)	118.9(3)
C(31)-N(4)-Cu(1)#1	113.36(16)	C(26)-C(27)-C(28)	119.9(3)
C(35)-N(4)-Cu(1)#1	127.14(18)	C(27)-C(28)-C(29)	122.6(3)
C(41)-N(5)-Cu(1)	166.0(4)	C(28)-C(29)-C(24)	117.8(2)
C(43)-N(6)-Cu(2)	165.8(2)	C(28)-C(29)-C(30)	119.5(2)
N(1)-C(1)-C(2)	122.0(3)	C(24)-C(29)-C(30)	122.6(2)
C(1)-C(2)-C(3)	118.6(3)	O(2)-C(30)-C(36)	107.0(2)
C(4)-C(3)-C(2)	119.6(3)	O(2)-C(30)-C(29)	107.91(19)
C(3)-C(4)-C(5)	119.6(2)	C(36)-C(30)-C(29)	112.2(2)
N(1)-C(5)-C(4)	120.5(2)	O(2)-C(30)-C(31)	107.43(19)
N(1)-C(5)-C(6)	114.9(2)	C(36)-C(30)-C(31)	108.8(2)
C(4)-C(5)-C(6)	124.6(2)	C(29)-C(30)-C(31)	113.3(2)
O(1)-C(6)-C(5)	106.47(19)	N(4)-C(31)-C(32)	121.7(2)
O(1)-C(6)-C(12)	110.8(2)	N(4)-C(31)-C(30)	114.6(2)
C(5)-C(6)-C(12)	109.22(19)	C(32)-C(31)-C(30)	123.7(2)
O(1)-C(6)-C(7)	108.11(19)	C(33)-C(32)-C(31)	118.9(3)
C(5)-C(6)-C(7)	109.5(2)	C(34)-C(33)-C(32)	119.5(3)
C(12)-C(6)-C(7)	112.6(2)	C(33)-C(34)-C(35)	118.3(3)
N(2)-C(7)-C(8)	121.6(2)	N(4)-C(35)-C(34)	123.2(3)
N(2)-C(7)-C(6)	114.4(2)	N(3)-C(36)-C(37)	121.0(2)
C(8)-C(7)-C(6)	124.0(2)	N(3)-C(36)-C(30)	114.6(2)
C(7)-C(8)-C(9)	119.4(3)	C(37)-C(36)-C(30)	124.4(2)
C(10)-C(9)-C(8)	119.1(3)	C(38)-C(37)-C(36)	119.4(3)
C(9)-C(10)-C(11)	118.5(3)	C(37)-C(38)-C(39)	119.7(3)
N(2)-C(11)-C(10)	122.8(3)	C(38)-C(39)-C(40)	118.8(3)
C(13)-C(12)-C(17)	118.2(2)	N(3)-C(40)-C(39)	121.8(3)
C(13)-C(12)-C(6)	121.7(2)	N(5)-C(41)-C(42)	177.0(6)
C(17)-C(12)-C(6)	120.0(2)	N(6)-C(43)-C(44)	179.3(3)

O(5)-S(1)-O(4)	115.29(13)	F(5)-C(53)-F(6)	105.3(3)
O(5)-S(1)-O(3)	115.14(14)	F(4)-C(53)-F(6)	107.0(3)
O(4)-S(1)-O(3)	114.49(13)	F(5)-C(53)-S(2)	111.4(2)
O(5)-S(1)-C(52)	103.04(11)	F(4)-C(53)-S(2)	114.4(2)
O(4)-S(1)-C(52)	103.76(12)	F(6)-C(53)-S(2)	111.8(2)
O(3)-S(1)-C(52)	102.70(14)	N(7)-C(54)-C(56)	176.1(5)
F(1)-C(52)-F(3)	106.7(2)	O(6B)-S(2B)-O(7B)	114.69(18)
F(1)-C(52)-F(2)	106.7(2)	O(6B)-S(2B)-O(8B)	115.23(18)
F(3)-C(52)-F(2)	105.3(2)	O(7B)-S(2B)-O(8B)	115.01(18)
F(1)-C(52)-S(1)	114.4(2)	O(6B)-S(2B)-C(53B)	102.91(16)
F(3)-C(52)-S(1)	111.83(19)	O(7B)-S(2B)-C(53B)	103.65(17)
F(2)-C(52)-S(1)	111.40(19)	O(8B)-S(2B)-C(53B)	102.93(14)
O(7)-S(2)-O(6)	114.77(18)	F(4B)-C(53B)-F(5B)	106.7(3)
O(7)-S(2)-O(8)	114.86(18)	F(4B)-C(53B)-F(6B)	106.9(3)
O(6)-S(2)-O(8)	115.27(18)	F(5B)-C(53B)-F(6B)	105.0(3)
O(7)-S(2)-C(53)	103.80(16)	F(4B)-C(53B)-S(2B)	114.3(2)
O(6)-S(2)-C(53)	102.86(16)	F(5B)-C(53B)-S(2B)	111.5(2)
O(8)-S(2)-C(53)	102.87(15)	F(6B)-C(53B)-S(2B)	111.9(2)
F(5)-C(53)-F(4)	106.5(3)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+1/2

Table A20. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **[*p*-LCu(II)$_2$]$_2$(4OTf)** (CCDC 812330). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	228(2)	151(2)	213(2)	-4(2)	26(1)	4(2)
Cu(2)	278(2)	167(2)	215(2)	-15(2)	40(1)	-14(2)
O(1)	169(10)	144(9)	197(10)	1(8)	40(8)	15(8)
O(2)	183(10)	164(9)	191(9)	15(8)	30(8)	15(8)
N(1)	201(13)	171(12)	212(12)	14(11)	0(10)	-9(10)
N(2)	174(13)	182(12)	239(13)	5(10)	-3(10)	11(10)
N(3)	291(14)	212(13)	256(13)	-65(11)	42(11)	-33(11)
N(4)	205(14)	217(12)	211(13)	-10(10)	49(10)	55(10)
N(5)	573(19)	162(13)	357(16)	-86(13)	-26(13)	176(14)
N(6)	371(16)	206(13)	304(15)	-69(12)	27(11)	16(12)
C(1)	360(19)	158(15)	287(17)	4(13)	14(14)	25(13)
C(2)	490(20)	203(16)	270(17)	87(13)	20(15)	27(15)
C(3)	377(19)	286(18)	198(15)	23(14)	37(13)	-12(14)
C(4)	250(17)	184(15)	248(16)	-16(13)	23(13)	5(12)
C(5)	142(15)	156(14)	231(15)	-5(12)	-4(12)	-20(11)
C(6)	126(15)	164(14)	204(14)	-14(12)	29(11)	3(11)
C(7)	180(16)	115(13)	237(15)	-3(12)	11(12)	1(12)
C(8)	237(17)	234(15)	257(15)	-15(13)	20(13)	-3(13)
C(9)	168(17)	328(17)	445(19)	-55(16)	90(14)	7(14)

C(10)	181(17)	360(19)	430(20)	-93(15)	-31(15)	49(14)
C(11)	300(19)	288(18)	276(16)	-30(13)	-52(14)	54(14)
C(12)	193(16)	149(13)	181(14)	18(11)	39(12)	-11(12)
C(13)	185(16)	199(15)	239(15)	25(12)	2(12)	0(12)
C(14)	283(18)	184(15)	243(16)	8(12)	30(13)	50(13)
C(15)	329(19)	151(14)	237(15)	-5(12)	-25(13)	-31(13)
C(16)	179(16)	217(15)	241(15)	1(12)	-26(12)	-14(12)
C(17)	193(16)	176(14)	169(14)	32(12)	35(12)	18(12)
C(18)	139(15)	154(13)	241(15)	-14(12)	-4(11)	-14(11)
C(19)	203(17)	273(16)	195(15)	-29(13)	21(12)	33(13)
C(20)	220(16)	264(16)	208(15)	52(13)	0(12)	78(13)
C(21)	109(14)	206(15)	241(15)	6(12)	22(11)	3(11)
C(22)	143(16)	265(16)	230(15)	38(13)	53(12)	31(12)
C(23)	185(16)	211(14)	237(15)	64(13)	15(12)	9(13)
C(24)	202(16)	196(14)	149(14)	25(12)	-39(12)	29(12)
C(25)	195(16)	264(16)	210(15)	21(13)	43(12)	14(13)
C(26)	210(17)	220(16)	301(17)	73(13)	-2(13)	-25(13)
C(27)	261(18)	183(15)	355(18)	44(13)	31(14)	51(13)
C(28)	220(17)	236(16)	260(16)	-3(13)	56(12)	40(13)
C(29)	179(16)	173(14)	172(14)	17(11)	-17(12)	14(12)
C(30)	191(15)	168(13)	127(13)	4(12)	-9(11)	3(12)
C(31)	175(16)	157(14)	219(15)	29(12)	33(12)	-5(11)
C(32)	221(18)	301(17)	254(16)	55(13)	12(13)	9(13)
C(33)	185(17)	340(18)	387(19)	97(15)	8(14)	17(14)
C(34)	219(18)	339(18)	357(18)	81(15)	100(14)	91(14)
C(35)	308(19)	303(17)	256(16)	15(14)	90(14)	49(14)
C(36)	164(16)	215(15)	255(16)	-14(13)	67(12)	-17(12)
C(37)	328(18)	283(17)	236(16)	3(13)	10(13)	-34(14)
C(38)	530(20)	410(20)	232(17)	-18(15)	-11(15)	-94(17)
C(39)	690(30)	350(20)	280(18)	-111(16)	21(17)	-152(18)
C(40)	540(20)	240(17)	358(19)	-47(15)	80(16)	-106(15)
C(41)	940(40)	1220(50)	610(30)	20(30)	-270(30)	10(40)
C(42)	3340(90)	1100(50)	1510(60)	-580(40)	-680(60)	1440(60)
C(43)	351(19)	277(17)	240(16)	-87(14)	45(14)	36(15)
C(44)	590(20)	249(17)	380(20)	3(15)	49(16)	105(16)
S(1)	660(6)	279(4)	397(5)	-100(4)	216(4)	-122(5)
F(1)	713(16)	1340(20)	971(19)	-441(17)	464(14)	102(16)
F(2)	514(14)	984(18)	696(15)	-159(14)	150(11)	-256(12)
F(3)	832(17)	1110(20)	595(15)	310(14)	282(12)	-199(15)
O(3)	1480(30)	318(15)	574(17)	25(13)	-16(17)	129(16)
O(4)	566(15)	332(12)	451(14)	-151(11)	262(11)	-100(11)
O(5)	847(18)	635(17)	451(15)	-296(13)	213(13)	-303(14)
C(52)	450(30)	730(30)	510(20)	-170(20)	180(20)	-110(20)
S(2)	1230(20)	440(17)	950(20)	3(14)	-586(18)	-151(15)
F(4)	1880(80)	310(40)	2090(80)	180(40)	-630(60)	170(40)
F(5)	3800(120)	1110(50)	1570(60)	-540(50)	940(70)	520(60)
F(6)	780(40)	620(50)	1470(70)	80(50)	200(40)	120(40)

O(6)	2450(110)	580(50)	2060(100)	400(60)	-1580(80)	-730(70)
O(7)	990(40)	520(30)	860(40)	30(30)	-100(30)	-250(30)
O(8)	2170(90)	460(50)	800(50)	180(40)	-960(50)	-240(50)
C(53)	1660(100)	100(30)	790(60)	-190(40)	320(60)	120(50)
N(7)	850(30)	1130(30)	490(20)	50(20)	160(20)	-70(20)
C(54)	520(30)	1000(40)	530(30)	20(30)	80(20)	-280(20)
C(56)	540(30)	960(30)	500(20)	200(20)	-25(19)	-230(20)
S(2B)	492(18)	282(17)	310(14)	-23(13)	-112(12)	68(14)
F(4B)	620(40)	210(40)	450(30)	-80(30)	-320(30)	100(30)
F(5B)	500(40)	540(60)	450(40)	-180(40)	150(40)	60(40)
F(6B)	540(30)	340(30)	280(30)	-60(20)	-10(20)	-10(20)
O(6B)	420(40)	1000(70)	260(30)	-140(40)	180(30)	-570(40)
O(7B)	930(60)	370(60)	380(40)	190(40)	-390(40)	60(50)
O(8B)	610(40)	400(30)	260(30)	-140(30)	-60(30)	140(30)
C(53B)	110(40)	160(40)	650(60)	100(40)	110(40)	110(30)

Table A21. Crystal Information and Atomic Parameters for **[*m*-LCu(II)$_2$]$_3$(6OTf)** (Preliminary structure).

Crystal system	triclinic
Space group	P -1 (2)
Cell parameters	a=14.1804(100) Å b=24.7886(57) Å c=24.9513(57) Å α=119.560(5)° β=94.867(7)° γ=100.384(7)°
Cell ratio	a/b=0.5721 b/c=0.9935 c/a=1.7596
Cell volume	7347.75(573) Å^3

Atomic Parameters

Atom	x/a	y/b	z/c	U (Å^2)
Cu5	0.02096	0.29131	0.69981	0.0281
Cu3	0.41856	0.08057	0.91034	0.0314
Cu6	-0.1918	0.31635	0.64326	0.0311
Cu1	0.36827	-0.02701	0.75479	0.0278
Cu4	0.02762	0.43111	0.75574	0.0359
Cu2	0.1959	0.04515	0.84386	0.0329
S3	0.2863	0.06159	0.48524	0.0374
S1	0.36732	-0.07599	0.84964	0.0996
O15	0.09547	0.3641	0.66232	-0.0122
S2	0.53518	0.48887	0.96243	0.1333
S4	0.1406	0.71965	0.92027	0.158
O14	0.02727	0.36637	0.7777	0.0167
O2	0.24435	0.00277	0.7671	0.0271
C39	0.05005	0.33084	0.89504	0.0274
C1	0.12176	-0.00295	0.68518	0.0154

O11	0.23994	0.07085	0.43614	0.0499
O9	0.21683	0.02278	0.49834	0.0764
C62	-0.27757	0.16879	0.59763	0.011
N10	-0.28231	0.21495	0.58054	0.0301
N9	0.00047	0.20955	0.61386	0.0233
O17	-0.10946	0.39977	0.7152	0.0513
N7	0.13842	0.48923	0.83515	0.0202
O6	0.47215	0.49143	0.91647	0.0236
C2	0.18439	0.03064	0.6656	0.0241
C40	0.34905	0.27384	0.96232	0.0125
F3	0.199	-0.14441	0.85773	0.1158
C114	-0.26684	0.27766	0.74826	0.021
N2	0.49101	-0.02779	0.72314	0.0256
C115	-0.37019	0.25327	0.7168	0.0152
C58	-0.04734	0.09285	0.51127	0.0282
F8	0.27421	0.17777	0.58559	0.0623
C3	0.62086	0.20029	0.90461	0.0099
C67	-0.09105	0.53325	0.69192	0.027
O4	0.42772	-0.08835	0.80594	0.1041
C4	0.14611	0.0618	0.63812	0.0167
O1	0.30653	0.11205	0.89719	0.0188
C5	0.29569	0.04545	0.67771	0.022
C68	-0.25849	0.43677	0.69271	0.0517
N11	-0.28378	0.36983	0.6447	0.0457
C63	-0.33378	0.12062	0.58279	0.0105
O10	0.36798	0.02584	0.46549	0.0538
O3	0.42575	-0.07562	0.90339	0.0568
C6	0.16745	-0.1969	0.55656	0.0368
C7	0.28157	-0.14307	0.84265	0.2674
C76	0.18252	0.551	0.86472	0.0409
C129	-0.16193	0.19885	0.69461	0.0302
C41	-0.07867	0.41043	0.94033	0.0261
O7	0.63494	0.53625	0.99275	0.0528
C54	0.18132	0.34427	0.80155	0.0156
C116	-0.41603	0.30574	0.72801	0.0123
C42	-0.0197	0.41322	0.90228	0.0134
C8	0.21306	-0.09337	0.65835	0.0459
C43	-0.07379	0.37741	0.96092	0.0482
C72	-0.0588	0.50024	0.71627	0.0437
C64	-0.355	0.19819	0.53199	0.0199
N6	0.02143	0.48418	0.72598	0.0352
C9	0.54495	0.08662	0.83764	0.0477
C10	0.55941	0.0313	0.7656	0.0152

C11	0.56543	0.14973	0.84308	0.0142
C117	-0.26175	0.39179	0.78932	0.0162
C65	-0.39945	0.10512	0.5352	0.0216
N8	0.14956	0.2965	0.74782	0.0102
N1	0.55907	0.08031	0.93158	0.036
C118	-0.16037	0.17795	0.79749	0.0356
C12	0.07875	-0.07241	0.73661	0.0273
C13	0.01742	-0.00935	0.68115	0.0395
C14	0.52492	0.16448	0.80417	0.013
F2	0.20698	-0.15827	0.77044	0.1346
N3	0.2926	-0.10221	0.68327	0.0142
O16	-0.12306	0.26522	0.6712	0.0321
C15	0.0478	0.05193	0.62718	0.019
O18	-0.10782	0.32473	0.57087	0.0822
C16	0.50858	-0.08017	0.66244	0.053
C119	-0.11352	0.13605	0.74828	0.0256
C17	0.49943	0.08501	0.68417	0.0378
C44	0.50333	0.34586	1.02885	0.0215
C45	-0.01788	0.33914	0.94371	0.0983
O8	0.54254	0.42304	0.94069	0.0626
N4	0.08604	-0.03278	0.80109	0.0302
C120	-0.14976	0.54891	0.92825	0.0227
C19	0.46051	0.11243	0.74438	0.0195
C46	0.20734	0.28983	0.92189	0.0637
C66	-0.41269	0.13794	0.50918	0.0393
C74	0.21597	0.49695	0.92975	0.0158
C77	0.23701	0.58258	0.92204	0.019
C121	-0.21462	0.23015	0.74898	0.0366
C122	-0.22235	0.33807	0.77993	0.0507
C20	0.64372	0.03798	0.74234	0.0509
C55	0.27226	0.36137	0.84283	0.0099
C21	0.05047	-0.05163	0.83556	0.0375
C22	0.35764	0.08868	0.73276	0.0167
C47	0.16998	0.18153	0.80337	0.014
C69	-0.37394	0.47334	0.68052	0.1479
C23	0.24807	-0.21085	0.58453	0.0164
N5	0.12709	0.10493	0.90115	0.0244
C128	-0.12486	0.14898	0.70092	0.0297
C24	0.44189	0.03168	0.62403	0.0466
C59	0.06459	0.19412	0.58228	0.026
C25	-0.02644	0.01429	0.64534	0.028
C56	0.33057	0.32183	0.81454	0.039
C26	0.53022	0.22342	0.81876	0.0041

C27	0.03301	0.09965	0.8852	0.0162
C48	0.04	0.38233	0.87866	0.0651
C123	-0.21835	0.21925	0.79488	0.0198
C78	0.15873	0.45608	0.86547	0.0307
C70	-0.28213	0.51004	0.72858	0.1386
C49	0.4137	0.3256	0.98796	0.0024
C57	0.30408	0.27595	0.7532	0.0428
C50	0.11823	0.27267	0.86186	0.074
C29	0.59988	-0.06404	0.6414	0.0673
F1	0.32355	-0.18823	0.80302	0.1815
C30	0.30728	-0.15608	0.64475	0.0249
C60	-0.08653	0.18307	0.60546	0.0318
C31	0.59735	0.07447	0.88445	0.0371
C124	-0.11355	0.57168	0.90387	0.0228
C125	-0.20577	0.46088	0.82843	0.0232
C32	0.68967	0.05482	0.88433	0.0473
C33	0.33723	0.01669	0.6208	0.0296
C73	0.08445	0.52366	0.71141	0.0554
O13	0.01493	0.68301	0.86858	0.5508
C71	0.06678	0.5589	0.68147	0.0748
C61	-0.1118	0.11912	0.55179	0.0203
O12	0.19757	0.7228	0.97957	0.2178
C51	0.25605	0.23546	0.89913	0.0585
C52	0.23601	0.18986	0.83948	0.0109
C34	0.13858	-0.13768	0.59973	0.0385
C131	-0.16597	0.48892	0.80771	0.0098
C75	0.25549	0.5584	0.9529	0.0222
O5	0.30781	-0.02039	0.87394	0.1001
C126	-0.21175	0.48704	0.89139	0.0165
C53	0.11648	0.21301	0.80486	0.0704
C36	0.19063	0.09319	0.83429	0.2439
C37	0.63128	0.25627	0.9148	0.0218
O19	0.44637	0.0557	0.83182	0.0262
N12	0.3654	0.10239	0.99373	0.0476
C96	0.58066	0.26899	0.87391	0.0163
C97	0.35595	0.22079	0.97858	0.018
C98	0.28684	0.15181	0.95665	0.0324
C99	0.16529	-0.03698	0.71045	0.0612
C100	0.18695	0.15359	0.94687	0.0272
C101	0.02798	-0.12688	0.697	0.0577
C102	0.30891	0.13574	1.00068	0.0187
C103	-0.02651	0.12347	0.91316	0.0797
C104	0.27316	0.16215	1.05675	0.0426

C105	0.38935	0.06569	1.02079	0.0293
C106	0.74275	0.05424	0.93662	0.0471
C107	0.68079	-0.00613	0.68277	0.0499
C108	0.03229	0.18039	0.96432	0.0881
C109	0.16727	0.21189	0.98984	0.0677
C110	-0.02973	-0.11014	0.80617	0.0438
C111	-0.03325	-0.15299	0.72837	0.0949
C112	0.69426	0.06587	0.9833	0.0229
C113	0.61198	0.07579	0.97883	0.0671
O20	0.10042	0.82182	0.92995	0.4351
C130	-0.10992	0.54634	0.83833	0.0296
C127	-0.36568	0.36934	0.76079	0.0422
C132	-0.1586	0.20731	0.64609	0.013
C133	0.10841	0.38584	0.8325	0.0263
C134	-0.15059	0.45907	0.7415	0.0692
C135	0.03935	0.13789	0.53024	0.0239
C136	0.21397	0.26529	0.72048	0.0355
C137	-0.03168	0.55509	0.66881	0.0829
C138	-0.38282	0.34343	0.61823	0.0812
C140	0.35837	0.1483	0.55494	0.0642
F9	0.39742	0.17991	0.54033	0.0641
F5	0.29522	0.7536	0.88828	0.2096
F4	0.26175	0.66667	0.84988	0.1957
F6	0.17696	0.7156	0.83314	0.2607
F7	0.39792	0.14535	0.60266	0.0622
C141	0.36952	0.08169	1.07926	0.0838
C142	0.31344	0.12021	1.08585	0.1031
C144	0.51878	0.30933	1.04971	0.0334
C146	0.15414	0.40438	0.70797	2
C145	-0.43163	0.40902	0.64077	0.0778
C143	0.45257	0.2492	1.03214	0.0192
C147	0.494	0.26456	0.43164	-0.0379
S5	0.05969	0.0167	0.01186	0.2291
C149	0.82932	0.96815	0.76342	-0.0009
O22	0.08705	0.02707	0.06676	0.1043
O21	0.12512	-0.0107	-0.02823	0.1482

Table A22. Crystal Information and Atomic Parameters for **[LCu(II)]$_2$(2OTf)** (Preliminary structure).

Crystal system	monoclinic
Space group	P 1 21/c 1 (14)
Cell parameters	a=12.1048(5) Å b=19.0115(7) Å c=22.7436(9) Å ß=92.885(2)°
Cell ratio	a/b=0.6367 b/c=0.8359 c/a=1.8789
Cell volume	5227.36(36) Å^3

Atomic Parameters

Atom	x/a	y/b	z/c	U (Å^2)
CU1	0.16682	1.01583	0.73216	
CU2	0.24292	0.95102	0.841	
O1	0.30128	0.97243	0.76393	
O2	0.10261	0.96495	0.79931	
N1	0.01534	1.05539	0.72729	
N2	0.25775	1.10541	0.75015	
N4	0.19128	1.04983	0.87717	
N5	0.39963	0.96053	0.86629	-1.2
C1	-0.0336	1.08908	0.68031	
H1	0.00633	1.09596	0.64587	-1.2
C2	-0.14009	1.11332	0.68198	
H2	-0.17407	1.13548	0.64827	-1.2
C3	-0.19809	1.10581	0.73209	
H3	-0.27106	1.12376	0.73401	-1.2
C4	-0.14699	1.07134	0.77952	
H4	-0.18501	1.06532	0.81471	
C5	-0.04071	1.04557	0.77596	
C6	0.0234	1.00652	0.82547	
C7	0.08431	1.06415	0.86415	-1.2
C8	0.03708	1.12648	0.88204	
H8	-0.03939	1.13504	0.87358	-1.2
C9	0.10089	1.17609	0.91211	
H9	0.06868	1.21844	0.92534	-1.2
C10	0.21179	1.16329	0.92261	
H10	0.2587	1.19757	0.94124	-1.2
C11	0.2533	1.09937	0.9054	
H11	0.32947	1.0898	0.91389	
C12	-0.052	0.96015	0.86118	-1.2
C13	-0.07285	0.97513	0.91922	
H13	-0.04618	1.01801	0.93603	-1.2
C14	-0.13153	0.92934	0.95352	
H14	-0.14627	0.94126	0.99293	-1.2
C15	-0.1686	0.86559	0.9294	
H15	-0.20717	0.833	0.95249	-1.2

C16	-0.14871	0.85065	0.87215	
H16	-0.17552	0.80747	0.85598	
C17	-0.09173	0.89509	0.83678	
C18	-0.07133	0.87252	0.77567	-1.2
C19	0.00611	0.82013	0.76644	
H19	0.04326	0.79878	0.79963	-1.2
C20	0.03107	0.79792	0.71053	
H20	0.08559	0.76285	0.70524	-1.2
C21	-0.02552	0.82821	0.66289	
H21	-0.00919	0.81404	0.62422	-1.2
C22	-0.10571	0.87887	0.67036	
H22	-0.14535	0.89848	0.63717	-1.2
C23	-0.12777	0.90088	0.72714	
H23	-0.18241	0.93588	0.7324	-1.2
C26	0.2183	1.17084	0.75137	
H26	0.14511	1.17941	0.736	-1.2
C27	0.28008	1.22693	0.77424	
H27	0.24943	1.27289	0.77529	-1.2
C28	0.38664	1.21436	0.79535	
H28	0.4313	1.25181	0.81073	-1.2
C29	0.42787	1.14725	0.79397	
H29	0.50169	1.13827	0.80815	
C30	0.36273	1.09254	0.7721	
C31	0.39759	1.01415	0.7691	
C32	0.45917	0.99502	0.82824	-1.2
C33	0.56865	1.01241	0.84177	
H33	0.61044	1.0368	0.81398	-1.2
C34	0.61607	0.99419	0.89544	
H34	0.69003	1.00758	0.90602	-1.2
C35	0.55599	0.95659	0.93357	
H35	0.58899	0.94156	0.97021	-1.2
C36	0.44642	0.94035	0.91866	
H36	0.40407	0.91485	0.94552	
C37	0.47277	0.99977	0.719	-1.2
C38	0.50134	1.05218	0.68003	
H38	0.47128	1.09794	0.68431	-1.2
C39	0.57134	1.04017	0.63565	
H39	0.58906	1.07727	0.60978	-1.2
C40	0.61607	0.97424	0.62854	
H40	0.66579	0.96568	0.59833	-1.2
C41	0.58712	0.92005	0.66653	
H41	0.6172	0.87442	0.6615	
C42	0.51644	0.93129	0.7108	

C43	0.48943	0.87146	0.7499	-1.2
C44	0.56278	0.85024	0.79436	
H44	0.63189	0.87374	0.79932	-1.2
C45	0.53939	0.7953	0.8326	
H45	0.59223	0.78118	0.86259	-1.2
C46	0.43881	0.76204	0.82613	
H46	0.41968	0.72632	0.853	-1.2
C47	0.36594	0.78084	0.78044	
H47	0.29798	0.75615	0.7749	-1.2
C48	0.38961	0.83491	0.74243	
H48	0.33803	0.8472	0.71126	
N6	0.19504	0.87563	0.89656	
C49	0.1539	0.83367	0.92309	-1.5
C50	0.09901	0.7797	0.95552	-1.5
H50A	0.02845	0.76772	0.93493	-1.5
H50B	0.08533	0.79703	0.99508	
H50C	0.14602	0.73776	0.95855	
C53	0.59861	0.20504	0.94288	
F1	0.53956	0.25904	0.92199	
F2	0.53036	0.14923	0.93997	
F3	0.61911	0.21731	1.00011	
O3	0.6812	0.17459	0.84538	
O4	0.78007	0.25652	0.91122	
O5	0.77351	0.13361	0.93607	
S1	0.72226	0.19077	0.9044	
C54A	0.32269	0.16578	0.52261	
F4A	0.3387	0.15675	0.46418	
F5A	0.34878	0.22925	0.53648	
F6A	0.39004	0.1222	0.55417	
O6A	0.17664	0.15532	0.59772	
O7A	0.11817	0.19246	0.49965	
O8A	0.17162	0.07028	0.5156	0.0446
S2A	0.1786	0.14324	0.5333	0.1532
C54B	0.28781	0.14436	0.5575	0.1747
F4B	0.28118	0.19771	0.59308	0.1371
F5B	0.30714	0.08917	0.58878	0.1211
F6B	0.37683	0.14906	0.52617	0.1399
O6B	0.08602	0.11098	0.54975	0.0915
O7B	0.19529	0.07413	0.47326	0.1329
O8B	0.14951	0.1961	0.48013	
S2B	0.1715	0.1328	0.50613	
N7D	0.71721	0.35908	1.04552	
C7D	0.67351	0.38489	1.00461	-1.5

C8D	0.62374	0.42049	0.9523	-1.5
H8DA	0.55777	0.39463	0.93789	-1.5
H8DB	0.67738	0.422	0.92146	
H8DC	0.60291	0.46854	0.96271	
N3A	0.1543	0.97371	0.6496	
C24A	0.12646	0.9514	0.60634	-1.5
C25A	0.0854	0.92175	0.5489	-1.5
H25A	0.00479	0.92671	0.54487	-1.5
H25B	0.10516	0.87183	0.54707	0.0965
H25C	0.11915	0.94713	0.51687	0.0918
N3B	0.19133	0.99313	0.65793	0.3353
C24B	0.22791	0.96016	0.62187	-1.5
C25B	0.24474	0.92444	0.56548	-1.5
H25D	0.24826	0.87349	0.57186	-1.5
H25E	0.31413	0.94063	0.54965	
H25F	0.18302	0.93544	0.53745	

Anisotropic displacement parameters (in $Å^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
CU1	0.01923	0.02334	0.02519	-0.00145	-0.00202	0.00017
CU2	0.01995	0.02155	0.02849	-0.0001	-0.00168	0.0035
O1	0.01793	0.00943	0.03298	0.00051	-0.00585	-0.00067
O2	0.01736	0.01669	0.02474	-0.00103	-0.00256	0.00127
N1	0.02446	0.02764	0.02425	-0.0036	-0.0012	0.00279
N2	0.01524	0.01233	0.03291	-0.00005	-0.00196	0.00018
N4	0.02105	0.0241	0.02063	-0.00399	0.006	0.002
N5	0.02122	0.01455	0.03216	-0.0009	-0.00558	-0.00094
C1	0.02582	0.0343	0.03132	-0.00456	-0.00249	0.00897
C2	0.0251	0.04042	0.02705	-0.00225	-0.00634	0.0104
C3	0.02501	0.02432	0.04921	0.0052	-0.00283	0.00737
C4	0.02561	0.02598	0.03034	0.00266	0.00036	0.00529
C5	0.01402	0.02176	0.032	-0.00419	-0.00028	0.00541
C6	0.01511	0.01671	0.02304	0.00127	-0.00379	-0.00011
C7	0.02646	0.01731	0.02291	0.00076	0.00896	0.00375
C8	0.0334	0.03096	0.02583	0.00489	0.00872	0.004
C9	0.05025	0.01998	0.02605	-0.00139	0.00905	-0.00419
C10	0.04481	0.02927	0.0218	-0.01807	0.00795	-0.00396
C11	0.02091	0.03146	0.02453	-0.01224	-0.00345	-0.0023
C12	0.01614	0.01727	0.02221	0.00241	-0.003	0.00919
C13	0.0173	0.01746	0.03524	-0.00091	-0.00237	0.0059
C14	0.02142	0.0398	0.02783	0.00978	0.00207	0.00995
C15	0.02009	0.02627	0.03408	-0.01066	-0.00216	0.01002

C16	0.02441	0.03091	0.03165	-0.01106	-0.00182	0.00245
C17	0.01591	0.0229	0.02518	-0.0024	-0.00541	0.00453
C18	0.02797	0.02758	0.02877	-0.01772	-0.00312	0.00075
C19	0.04923	0.04015	0.03342	-0.02004	-0.001	-0.01121
C20	0.07542	0.05649	0.04939	-0.01908	0.01068	-0.02176
C21	0.11311	0.05188	0.03867	-0.03818	0.0211	-0.01739
C22	0.07556	0.04405	0.03929	-0.03671	-0.00657	0.00588
C23	0.05869	0.03091	0.02821	-0.03038	-0.00113	-0.00305
C26	0.01844	0.02045	0.03501	0.0049	-0.00061	0.00839
C27	0.0266	0.01183	0.04336	0.002	0.00208	0.00495
C28	0.02799	0.01972	0.03106	-0.00443	-0.00309	0.0019
C29	0.01474	0.02223	0.02396	-0.00124	-0.00534	0.00401
C30	0.01562	0.02147	0.01797	-0.00354	0.00098	0.00103
C31	0.01449	0.01886	0.02449	-0.00252	-0.0016	0.00167
C32	0.01977	0.00846	0.02153	0.00444	0.00329	0.00057
C33	0.0229	0.0149	0.02416	0.00259	-0.00218	0.00077
C34	0.02178	0.021	0.03863	-0.00041	-0.00284	-0.0012
C35	0.02931	0.02726	0.03313	0.00923	-0.01357	0.0009
C36	0.0375	0.02577	0.02152	0.00129	0.00137	0.00576
C37	0.01601	0.01844	0.02124	-0.00092	-0.00422	-0.0021
C38	0.02241	0.02538	0.02844	0.0074	-0.00154	-0.00535
C39	0.03202	0.03198	0.02751	-0.00931	0.00434	0.00154
C40	0.03574	0.04494	0.03279	-0.00236	0.01164	-0.00847
C41	0.03912	0.03209	0.03547	0.00116	0.00834	0.0005
C42	0.0158	0.03607	0.01956	-0.00209	-0.00105	-0.00575
C43	0.0287	0.01709	0.03076	0.00403	0.00593	-0.0027
C44	0.04027	0.02516	0.03936	0.00106	0.00551	-0.00938
C45	0.06795	0.02602	0.03799	0.01303	0.00842	0.00036
C46	0.06719	0.01402	0.06942	0.00291	0.02561	0.00566
C47	0.0482	0.01528	0.07467	-0.00529	0.01455	-0.00008
C48	0.03996	0.01848	0.04708	0.00635	0.00399	-0.00618
N6	0.02289	0.03634	0.0311	-0.00161	-0.00564	0.00837
C49	0.01699	0.02575	0.03356	0.00333	-0.00943	0.0098
C50	0.03396	0.03688	0.04154	-0.00283	-0.00484	0.01564
C53	0.03692	0.0287	0.0338	-0.00206	-0.00929	0.00155
F1	0.05648	0.06225	0.07045	0.02763	-0.01137	-0.00846
F2	0.03938	0.07944	0.0535	-0.01089	0.00246	0.00169
F3	0.05267	0.08876	0.03182	-0.0086	0.00153	-0.00752
O3	0.03742	0.06868	0.0385	-0.01295	0.00272	-0.02765
O4	0.04693	0.04188	0.05038	-0.02636	-0.00792	-0.00023
O5	0.04282	0.02866	0.09764	0.00501	-0.0279	-0.00642
S1	0.02615	0.03355	0.0476	-0.00301	0.00067	-0.01014
C54A	0.04558	0.0569	0.05995	0.03744	0.01493	0.01402

F4A	0.1121	0.0822	0.09381	-0.02125	0.0561	-0.04501
F5A	0.04664	0.04085	0.06872	0.00094	-0.01884	-0.01768
F6A	0.06637	0.08769	0.20393	0.00966	-0.06311	0.06948
O6A	0.15202	0.09201	0.03449	-0.05633	0.04832	-0.00313
O7A	0.02768	0.03211	0.08265	0.01682	0.00999	0.0283
O8A	0.08129	0.01453	0.11811	-0.00932	-0.03463	0.01497
S2A	0.04797	0.02574	0.05141	0.00186	0.00299	0.01736
N7D	0.07887	0.07508	0.03624	0.02678	-0.00198	-0.01659
C7D	0.05354	0.07788	0.04888	0.00573	0.0143	-0.02049
C8D	0.06812	0.09196	0.05908	0.02014	-0.03048	0.01551
N3A	0.03133	0.01871	0.01885	0.00147	-0.01047	-0.00791
C24A	0.04051	0.02012	0.02987	0.01131	-0.00497	-0.00144
C25A	0.08836	0.04173	0.03431	-0.00849	-0.00918	-0.01555

Table A23. Crystal Information and Atomic Parameters for **[LCu(II)]$_3$(3OTf)** (Preliminary structure).

Crystal system	monoclinic
Space group	P 1 21/n 1 (14)
Cell parameters	a=13.2490(23) b=26.0607(36) c=23.0766(42) β=104.580(5)°
Cell ratio	a/b=0.5084 b/c=1.1293 c/a=1.7418
Cell volume	7711.26(222) Å^3

Atom	x/a	y/b	z/c	U
Cu1	0.23137	0.26372	0.58153	
Cu2	0.40949	0.18098	0.68372	
Cu3	0.43582	0.29881	0.69366	
S2	0.06603	0.01368	0.33678	
S1	0.43615	0.22271	0.82939	
N7	0.35407	0.35075	0.72542	
O1	0.39937	0.23584	0.76576	
C2	0.2875	0.37744	0.68018	
C3	0.62262	0.25711	0.61568	
F1	0.33384	0.20378	0.91039	
N2	0.31898	0.13019	0.70867	
F2	0.25722	0.25793	0.84238	
O4	0.48142	0.23884	0.65982	
F3	0.25703	0.17681	0.8215	
O3	0.48621	0.26501	0.86657	
O6	0.27699	0.21098	0.64258	

N5	0.16325	0.20254	0.53545
C4	0.21583	0.41259	0.6929
C5	0.60481	0.22903	0.56019
O5	0.33371	0.31214	0.61989
O2	0.48636	0.17344	0.84049
N1	0.54952	0.14737	0.69672
C6	0.59206	0.23494	0.66906
C7	0.39423	0.39802	0.60673
C8	0.61145	0.13509	0.53751
C9	0.72175	0.159	0.68086
C10	0.66405	0.30778	0.61829
N8	0.58325	0.30049	0.74281
C12	0.68965	0.33089	0.56866
C13	0.62358	0.17724	0.68202
C14	0.62213	0.33332	0.7895
C15	0.63235	0.25185	0.51035
C16	0.1615	0.41898	0.55014
C17	0.31613	0.21448	0.85205
N4	0.15837	0.32672	0.54397
C18	0.203	0.37116	0.56865
C19	0.07176	0.32856	0.49811
C20	0.02746	0.37573	0.47606
C21	0.3512	0.09509	0.75365
C22	0.30363	0.36462	0.61856
C23	0.74676	0.10768	0.69933
C24	0.45388	0.08229	0.51399
C25	0.57276	0.09705	0.71244
C26	0.55218	0.17729	0.54864
C27	0.64499	0.2657	0.72602
C28	0.39635	0.12437	0.52587
C29	0.67549	0.30211	0.51436
C30	0.562	0.08728	0.51914
C31	0.75037	0.25957	0.75632
C32	-0.00814	0.21186	0.62201
C33	0.35362	0.35896	0.78243
C34	0.1563	0.1624	0.57158
C35	0.0998	0.21296	0.65234
O9	0.02594	0.06128	0.30722
O7	0.06102	-0.02974	0.29757
O8	0.0365	0.0039	0.39179
F4	0.24686	0.03934	0.31629
C36	0.49991	0.42665	0.54135
C37	0.53844	0.45763	0.64483

C38	0.06883	0.28423	0.71469
C39	0.2849	0.3932	0.79854
C40	0.13596	0.24903	0.69856
C41	0.10348	0.14815	0.45006
C42	0.1416	0.10375	0.69845
C43	0.41957	0.3977	0.55083
C44	0.13658	0.19597	0.475
C45	0.17434	0.06592	0.74256
C46	0.09753	0.10636	0.4876
C47	0.35981	0.36466	0.49791
C48	0.18671	0.17889	0.63743
C49	-0.07563	0.2483	0.63803
C50	0.21397	0.13488	0.68233
C51	0.28168	0.06168	0.77048
C52	0.79082	0.29187	0.80463
C53	0.28869	0.38952	0.45033
C54	-0.03977	0.28507	0.68455
F5	0.25892	-0.01479	0.38839
F6	0.22739	0.06458	0.40218
C55	0.20577	0.02589	0.36189
C56	-0.08865	0.12608	0.58258
C57	0.38206	0.31236	0.49678
C58	0.67216	0.07751	0.71561
C59	0.23494	0.35924	0.40241
C60	0.0709	0.42098	0.50226
C61	0.25285	0.30591	0.40074
C62	0.12508	0.11372	0.55028
C63	0.44373	0.17233	0.54326
C64	-0.16903	0.1142	0.47571
C65	-0.1408	0.09445	0.53389
C66	0.32879	0.28204	0.44772
C67	0.56017	0.45691	0.58937
C68	-0.09137	0.19764	0.51397
C69	0.21503	0.4209	0.75236
C70	0.72784	0.32996	0.82135
C71	-0.06175	0.1762	0.57213
C72	0.45496	0.42864	0.65303
C73	-0.14427	0.16533	0.4657
O10	0.11112	0.43434	0.87366
C78	0.07135	0.34577	0.87054
C79	0.02512	0.39897	0.85741
C80	0.08005	0.48677	0.86595
C81	0.1813	0.51868	0.88706

O11	0.61695	0.39052	0.38716	
C84	0.76953	0.43376	0.4451	
C87	0.5086	0.38977	0.35442	
C88	0.65798	0.44043	0.41267	
C89	0.48606	0.33446	0.32894	
F9	0.17858	0.57308	0.33507	
O14	-0.03751	0.50306	0.3786	
F7A	0.08342	0.59663	0.39087	
F8A	0.62995	0.01445	0.59266	0.30589
O12A	0.67564	0.14774	0.48782	0.40345
S3A	0.05064	0.50179	0.35368	
C95B	0.09171	0.56824	0.35182	
F8B	0.29051	0.1598	0.55445	0.42516
F7B	0.30353	0.55337	0.45262	0.53674
O19A	0.57245	0.0512	0.48181	0.30156
O12B	0.45638	0.11687	0.45951	0.36105
O19B	0.43588	-0.00208	0.50275	0.28376

Anisotropic displacement parameters (in $Å^2$)

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Cu1	0.01331	0.01207	0.01087	0.00158	0.0008	0.00061
Cu2	0.01157	0.01156	0.01311	0.00082	0.0016	0.00109
Cu3	0.01212	0.01236	0.01161	0.00262	0.00008	-0.00058
S2	0.02133	0.01433	0.02801	0.0039	0.00419	0.00178
S1	0.01687	0.01709	0.01014	-0.00162	-0.00083	-0.00001
N7	0.00645	0.01059	0.0161	-0.00113	0.00112	0.00318
O1	0.0153	0.01538	0.01341	-0.00488	0.00107	-0.00455
C2	0.01326	0.01335	0.01515	-0.00801	-0.00042	-0.00187
C3	0.00348	0.02568	0.01365	0.00874	0.00344	0.00318
F1	0.03886	0.03739	0.01313	-0.00143	0.00726	0.00491
N2	0.0159	0.01132	0.01081	-0.00018	0.0048	-0.00398
F2	0.021	0.03041	0.02288	0.00104	0.00666	-0.00584
O4	0.00944	0.01072	0.01045	0.00049	0.00191	-0.00129
F3	0.02406	0.02833	0.03248	-0.00916	0.01302	-0.00832
O3	0.0232	0.02193	0.01433	-0.00582	-0.00516	-0.00629
O6	0.00697	0.01289	0.00999	-0.00301	-0.0018	0.00004
N5	0.00688	0.01662	0.01129	0.00141	0.0004	-0.00313
C4	0.01575	0.01013	0.02378	-0.00204	0.00657	-0.00571
C5	0.00435	0.02248	0.0171	0.00785	0.00053	0.00062
O5	0.00899	0.009	0.0102	0.00151	-0.0035	-0.00072
O2	0.01814	0.01612	0.02255	0.00343	-0.0039	-0.00026
N1	0.00884	0.01559	0.01179	0.00008	0.00007	-0.00096
C6	0.00874	0.01241	0.01233	0.00112	0.00204	-0.00202

C7	0.01197	0.01134	0.01829	0.00847	-0.00039	0.01012
C8	0.02945	0.01845	0.0199	0.00825	0.01036	0.00309
C9	0.00913	0.02601	0.01484	0.00644	-0.00063	-0.00173
C10	0.00484	0.01489	0.02201	0.00238	0.00186	0.00132
N8	0.01173	0.01029	0.01406	-0.00094	0.00037	0.00397
C12	0.0078	0.02917	0.01787	0.00682	0.00118	-0.00041
C13	0.01795	0.01357	0.00653	0.00178	-0.00358	-0.00271
C14	0.01802	0.02107	0.01758	-0.00845	0.00275	0.00118
C15	0.00717	0.0245	0.02452	0.00097	0.0069	0.00249
C16	0.01988	0.01657	0.0119	0.01124	0.0044	0.00528
C17	0.03356	0.01571	0.01662	-0.00144	0.00793	-0.00008
N4	0.01421	0.01623	0.00951	0.00376	0.0009	0.0035
C18	0.01735	0.02053	0.00469	0.00138	0.00491	0.00002
C19	0.00827	0.03116	0.01312	0.00461	-0.00055	-0.00316
C20	0.01999	0.02241	0.02078	0.00644	0.00761	-0.00025
C21	0.02891	0.0066	0.01022	0.0048	0.00334	0.00132
C22	0.01122	0.01449	0.01252	0.00225	0.00298	0.00372
C23	0.0192	0.02069	0.01953	0.00292	-0.00195	-0.00351
C24	0.02496	0.0232	0.01625	0.00001	-0.00024	0.00007
C25	0.02632	0.01435	0.01347	0.01122	-0.00349	0.0004
C26	0.0236	0.01694	0.00496	-0.00287	0.00081	-0.00117
C27	0.01407	0.0091	0.01491	-0.00357	0.00776	0.00244
C28	0.02157	0.02481	0.0161	-0.00247	0.00121	0.00161
C29	0.01012	0.02636	0.03196	0.00341	0.00591	0.01099
C30	0.02952	0.01855	0.0202	-0.00273	-0.00139	0.00072
C31	0.01352	0.02307	0.0156	-0.00966	-0.00199	0.0007
C32	0.01053	0.01378	0.01337	-0.00268	0.00063	0.00154
C33	0.01741	0.01137	0.01781	-0.0098	0.0073	-0.00578
C34	0.00504	0.01935	0.00993	0.00261	0.00146	0.0022
C35	0.01343	0.01134	0.016	-0.00075	0.00802	0.0023
O9	0.02252	0.02619	0.05048	0.00722	0.00386	0.01135
O7	0.01912	0.02531	0.04134	0.00281	-0.00025	-0.01211
O8	0.02674	0.03472	0.03695	-0.00185	0.01021	0.0052
F4	0.02715	0.03144	0.03802	-0.00095	0.01107	-0.00166
C36	0.02231	0.0248	0.03514	-0.00781	0.00841	0.01343
C37	0.01517	0.0289	0.03703	0.00308	0.00505	0.01619
C38	0.02421	0.02116	0.01757	-0.00072	0.01067	0.00079
C39	0.01341	0.01637	0.02238	-0.00407	0.00695	-0.00347
C40	0.02755	0.01303	0.01366	-0.00211	0.01189	0.0002
C41	0.00765	0.0284	0.01423	0.00653	-0.00156	-0.00207
C42	0.01992	0.01435	0.01614	-0.00719	0.0064	-0.00097
C43	0.01963	0.01342	0.0161	0.00183	-0.00116	0.00776
C44	0.00699	0.01945	0.01088	0.00663	-0.00378	-0.00185

C45	0.02483	0.01483	0.01654	0.00066	-0.00344	0.00078
C46	0.0051	0.02462	0.01445	0.00454	0.00073	0.00177
C47	0.01688	0.03339	0.0168	-0.00074	0.00826	0.00229
C48	0.00589	0.01621	0.01179	0.00089	-0.00251	0.00029
C49	0.02315	0.01852	0.02103	0.00174	0.01367	0.00181
C50	0.01366	0.01759	0.00567	0.00559	-0.00599	-0.00286
C51	0.02008	0.01287	0.01336	-0.00627	0.00409	0.0002
C52	0.02657	0.02062	0.02752	-0.00096	0.00551	0.00134
C53	0.00978	0.04152	0.00961	0.00628	0.00184	0.0015
C54	0.02667	0.01869	0.02818	-0.00028	0.012	0.00663
F5	0.02247	0.02699	0.03462	0.00564	-0.00501	0.00665
F6	0.02969	0.03034	0.03806	-0.00375	0.00312	-0.01306
C55	0.02715	0.0132	0.02876	0.00131	0.00702	-0.00384
C56	0.00849	0.01404	0.02586	-0.002	0.00487	0.00027
C57	0.02229	0.02039	0.02191	0.00122	0.0152	0.00278
C58	0.01602	0.02347	0.01862	0.00569	0.00141	-0.00166
C59	0.01947	0.04591	0.02845	0.0032	0.01407	-0.00024
C60	0.01749	0.02511	0.01545	0.00639	0.00397	-0.00213
C61	0.02328	0.03966	0.01972	0.00759	0.01161	-0.00062
C62	0.00473	0.02187	0.01725	-0.00061	-0.00006	-0.00817
C63	0.01008	0.01854	0.01097	-0.00296	0.00137	0.00149
C64	0.01566	0.02491	0.02287	0.00481	0.0095	0.00647
C65	0.00501	0.03022	0.01561	0.00094	-0.00007	0.00087
C66	0.01756	0.04485	0.01227	0.00189	0.00903	-0.00111
C67	0.02582	0.03475	0.03405	-0.00718	0.00154	0.01082
C68	0.0067	0.0258	0.01577	0.00527	-0.00138	0.00491
C69	0.01535	0.01914	0.02013	-0.00409	0.00352	-0.00804
C70	0.01705	0.02892	0.02397	-0.00541	0.00032	0.00097
C71	0.00489	0.02644	0.01623	0.0015	-0.00056	-0.00421
C72	0.0181	0.01006	0.02245	0.00272	-0.00315	0.00597
C73	0.01158	0.03388	0.01913	0.00205	0.00123	0.00258
O10	0.02803	0.02639	0.02258	0.00556	0.00789	0.00551
C78	0.03657	0.02011	0.04622	-0.0173	-0.0037	0.00055
C79	0.01805	0.04211	0.04136	-0.00764	-0.00926	-0.00058
C80	0.05777	0.02117	0.03693	0.02018	0.01281	0.01118
C81	0.06394	0.01789	0.04353	-0.00771	0.02394	-0.00278
O11	0.05194	0.07163	0.06778	0.01082	0.01528	0.02628
C84	0.04113	0.04174	0.09452	-0.00068	-0.01172	0.02176
C87	0.03526	0.11553	0.07674	-0.00881	0.01347	0.01638
C88	0.09591	0.02627	0.08534	-0.00102	0.05001	-0.00219
C89	0.04377	0.09622	0.09044	-0.02791	0.00215	-0.00245
F9	0.03382	0.08171	0.05889	-0.02358	0.00797	0.00172
O14	0.0271	0.02871	0.0328	0.00183	0.00419	-0.00307

F7A	0.18162	0.05357	0.24338	-0.04989	0.15431	-0.044
F8A	0.01672	0.03754	0.11046	0.00072	-0.02006	0.0455
O12A	0.03844	0.07176	0.1304	0.0347	0.01422	0.06206
S3A	0.04356	0.01948	0.04882	0.01284	0.02339	0.0092
C95B	0.0789	0.09012	0.06036	-0.06408	0.04915	-0.05826
F8B	0.09024	0.0687	0.04495	-0.06796	0.0027	-0.03017
F7B	0.79494	1.01756	1.96415	0.48947	1.08324	1.31463
O19A	0.07222	0.05629	0.05036	-0.03022	0.03805	-0.02671
O12B	0.10217	0.11369	0.09627	0.05754	0.04878	0.02166
O19B	0.05279	0.05125	0.01942	-0.02492	-0.0025	-0.00864

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A p p e n d i x B

Chapter 2 Supporting Information:
Toward CO_2 Reduction Chemistry with
Terphenyl Diphosphine Rhenium Complexes

Experimental Details

General considerations. All air- and moisture-sensitive compounds were manipulated using standard Schlenk techniques or in a glove box under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried using the method of Grubbs.[1] Benzene-d_6 was purchased from Cambridge Isotopes and vacuum transferred from sodium benzophenone ketyl. Unless indicated otherwise, all commercial chemicals were used as received. *Tert*-butyllithium solution in THF was purchased from Alfa. ^{1}H-NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer. Proton chemical shifts are reported with respect to internal solvent (7.16 ppm for C_6D_6) while ^{31}P shifts are reported with respect to 85% *aq.* H_3PO_4 external reference.

Synthesis of *m*-$P_2ReCl(CO)_2$: Ligand ***m*-P_2** (synthesized following literature procedure[2]) (0.25 g, 0.541 mmol) was dissolved in 5-6 mL xylene in a small Schlenk flask. Solid $ReCl(CO)_5$ (0.196 g, 0.541 mmol) was added and the suspension was heated at 130°C for 24 h to afford a soluble dark yellow solution. The solution was degassed to remove CO, then filtered through a glass paper plug in a glovebox. Recrystallization was achieved by vapor diffusion of hexane. Yield: 62.4%. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.67(m, 3H, *central aryl*), 7.52 (t, J=6.5 Hz, 2H, *aromatic arm*), 7.44 (t, J=7.3 Hz, 2H, *aromatic arm*), 7.19 (dd, J=7.5, 1.5 Hz, 2H, *aromatic arm*), 7.12 (dd, J=7.6, 1.6 Hz, 2H, *aromatic arm*), 6.55 (s, 1H, *central aryl*), 3.21 (m, 2H, *methyne*), 2.39 (m, 2H, *methyne*), 1.64 (m, 12H, *isopropyl CH_3*), 1.04 (m, 12H, *isopropyl CH_3*). ^{31}P NMR (300 MHz, CD_2Cl_2) δ 26.41 (s).

Synthesis of *p*-$P_2ReCl(CO)_2$: Ligand ***p*-P_2** (synthesized following literature procedure[3]) (0.01 g, 0.021 mmol) was dissolved in 2 mL xylene in a small Schlenk flask. Solid $ReCl(CO)_5$ (0.0078 g, 0.0211 mmol) was added and the suspension was heated at 130°C for 6 days to afford a soluble yellow solution. The solution was degassed to remove CO, then filtered through a glass paper plug in a glovebox. Recrystallization was achieved by vapor diffusion of hexane. Yield: 64%. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.85 (m, 2H), 7.67 (m, 2H), 7.59 (m, 4H), 7.36 (s, 2H), 6.19 (m, 2H), 3.33 (m, 2H), 2.70 (m, 2H), 1.72 (m, 6H), 1.52 (m, 6H), 0.98 (m, 6H), 0.78 (m, 6H). ^{31}P NMR (300 MHz, CD_2Cl_2) δ 8.16 (s).

Synthesis of [(*m*-$P_2(N(Me)_2)ORe(CO)_3$)]: Ligand ***m*-$P_2(N(Me)_2OMe)$** (synthesized following literature procedure[4]) (0.04 g, 0.075 mmol) was dissolved in 3 mL xylene in a small Schlenk flask. Solid $ReCl(CO)_5$ (0.027 g, 0.075 mmol) was added and the suspension was heated at 130°C for 30 h to afford a soluble yellow solution. The solution was degassed to remove CO, then filtered through a glass paper plug in a glovebox. Recrystallization was achieved by vapor diffusion of hexane. Yield: 37.5%. ^{31}P NMR (300 MHz, C_6D_6) δ 32.29 (s).

Reaction with *m*-P_2((*t*-Bu)OMe) and $ReCl(CO)_5$: Ligand ***m*-P_2((*t*-Bu)OMe)** (synthesized following literature procedure[4]) (0.04 g, 0.073 mmol) was dissolved in 3 mL xylene in a small Schlenk flask. Solid $ReCl(CO)_5$ (0.026 g, 0.073 mmol) was added and the suspension was heated at 130°C for 36 h to afford a soluble yellow solution. The solution was degassed to remove CO, then filtered through a glass paper plug in a glovebox. ^{31}P NMR (300 MHz, C_6D_6) δ 31.95(s), -1.69 (s, *free ligand*), -2.94 (s, *free ligand*).

Nuclear Magnetic Resonance Spectra

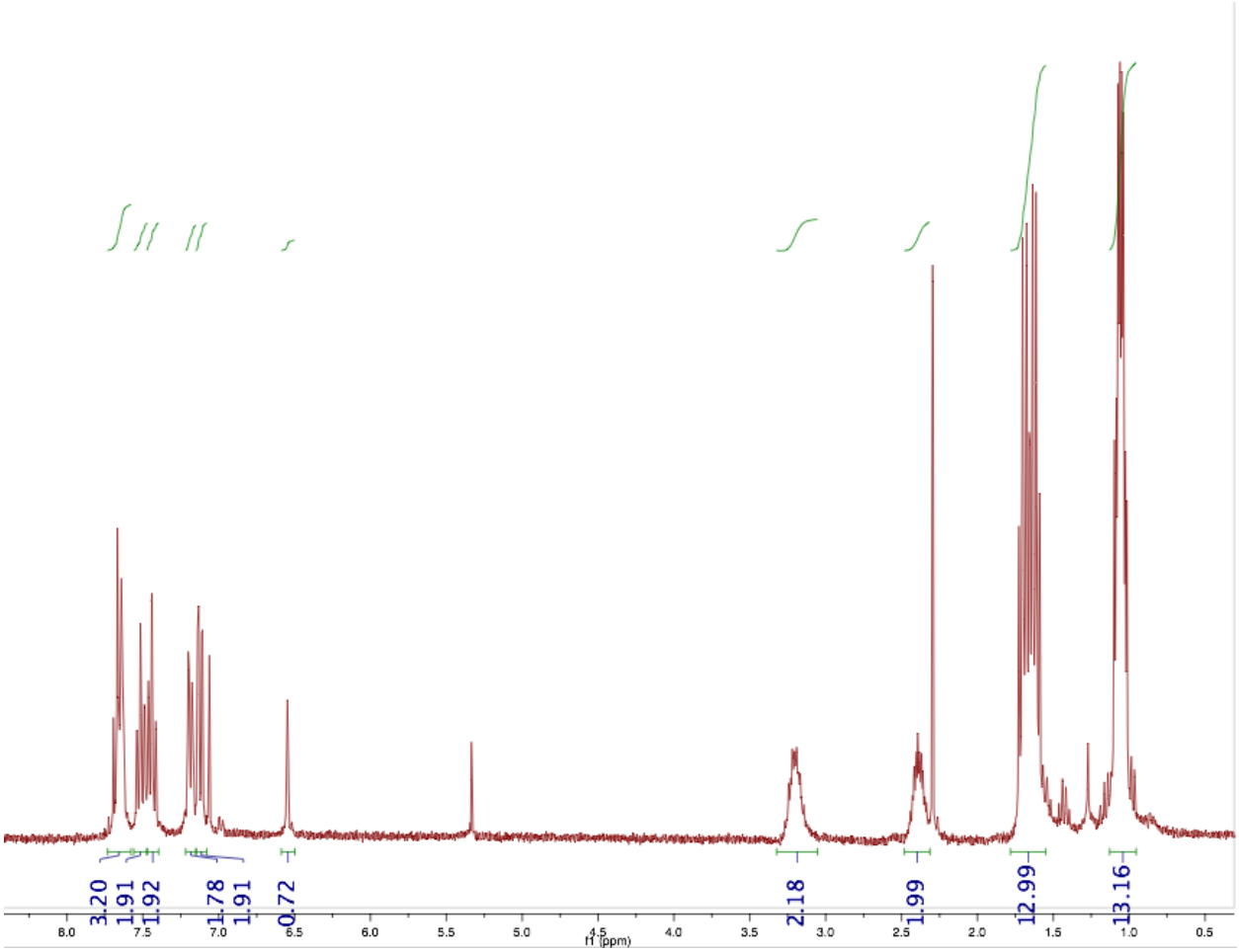

Figure B1. ^1H NMR (300 MHz, 25°, C_6D_6) of ***m*-$P_2ReCl(CO)_2$**.

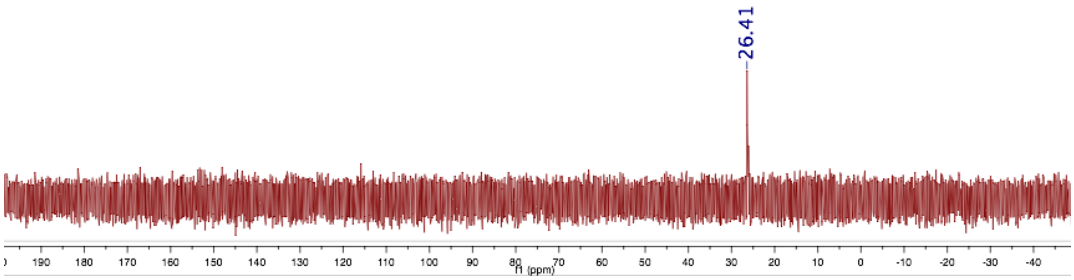

Figure B2. ^{31}P NMR (300 MHz, 25°, C_6D_6) of ***m*-$P_2ReCl(CO)_2$**.

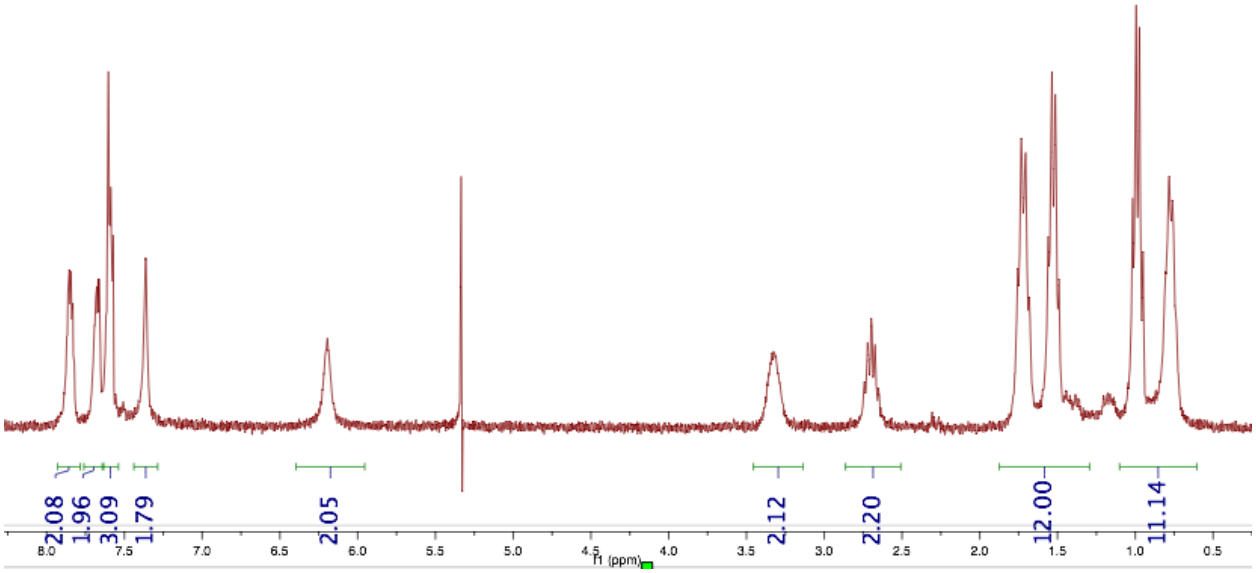

Figure B3. ^{1}H NMR (300 MHz, 25°, C_6D_6) of ***p*-P_2ReCl(CO)$_2$**.

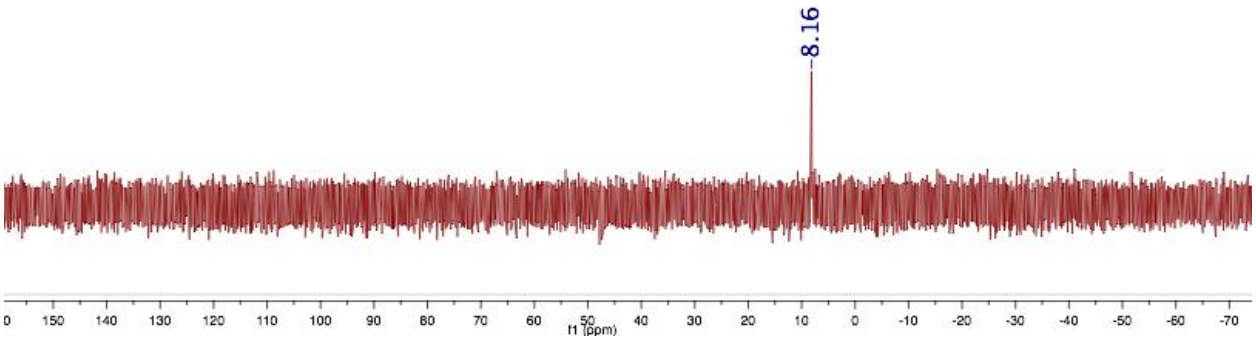

Figure B4. ^{31}P NMR (300 MHz, 25°, C_6D_6) of ***p*-P_2ReCl(CO)$_2$**.

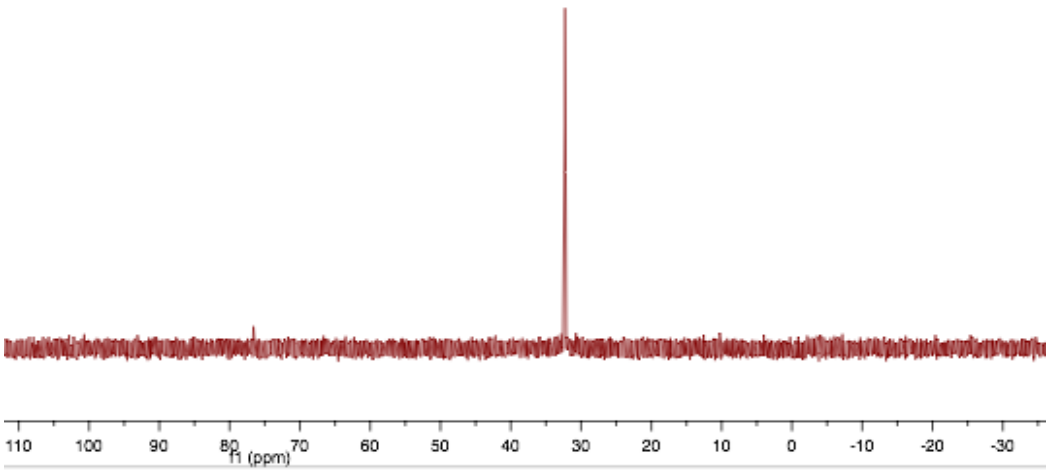

Figure B5. ^{31}P NMR (300 MHz, 25°, C_6D_6) of **[(*m*-P_2(N(Me)$_2$)ORe(CO)$_3$)]**.

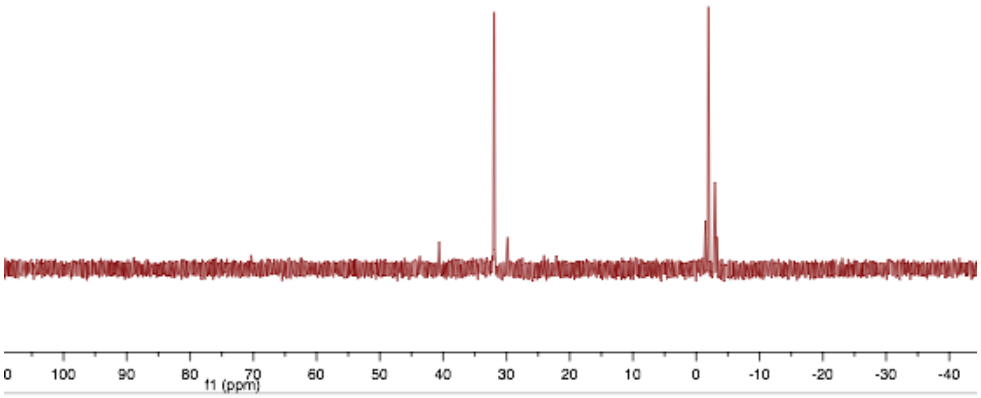

Figure B6. ^{31}P NMR (300 MHz, 25°, C_6D_6) of **[(*m*-P_2(*t*-Bu)ORe(CO)$_3$)]** and suspected free ligand.

IR Spectroscopy

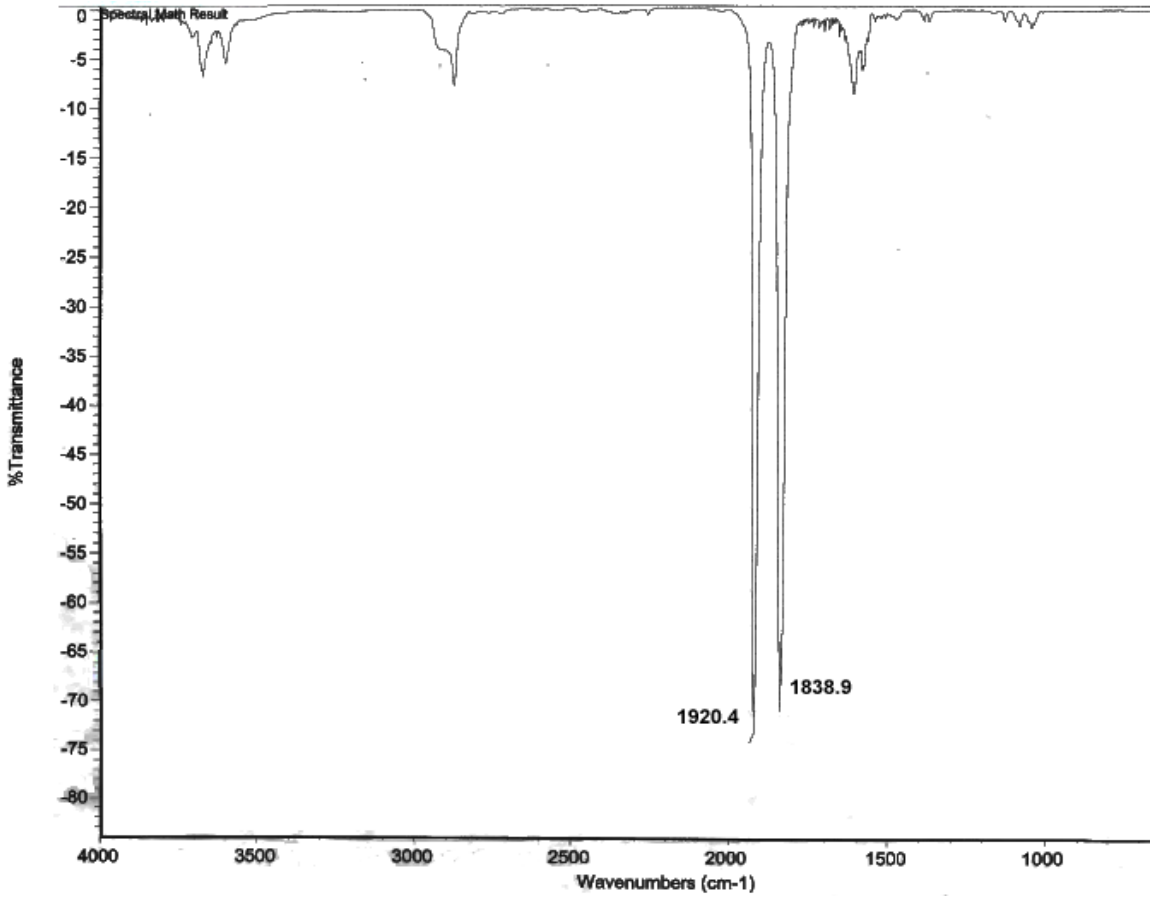

Figure B6. Solution IR (DCM) of ***m*-P_2ReCl(CO)$_2$**.

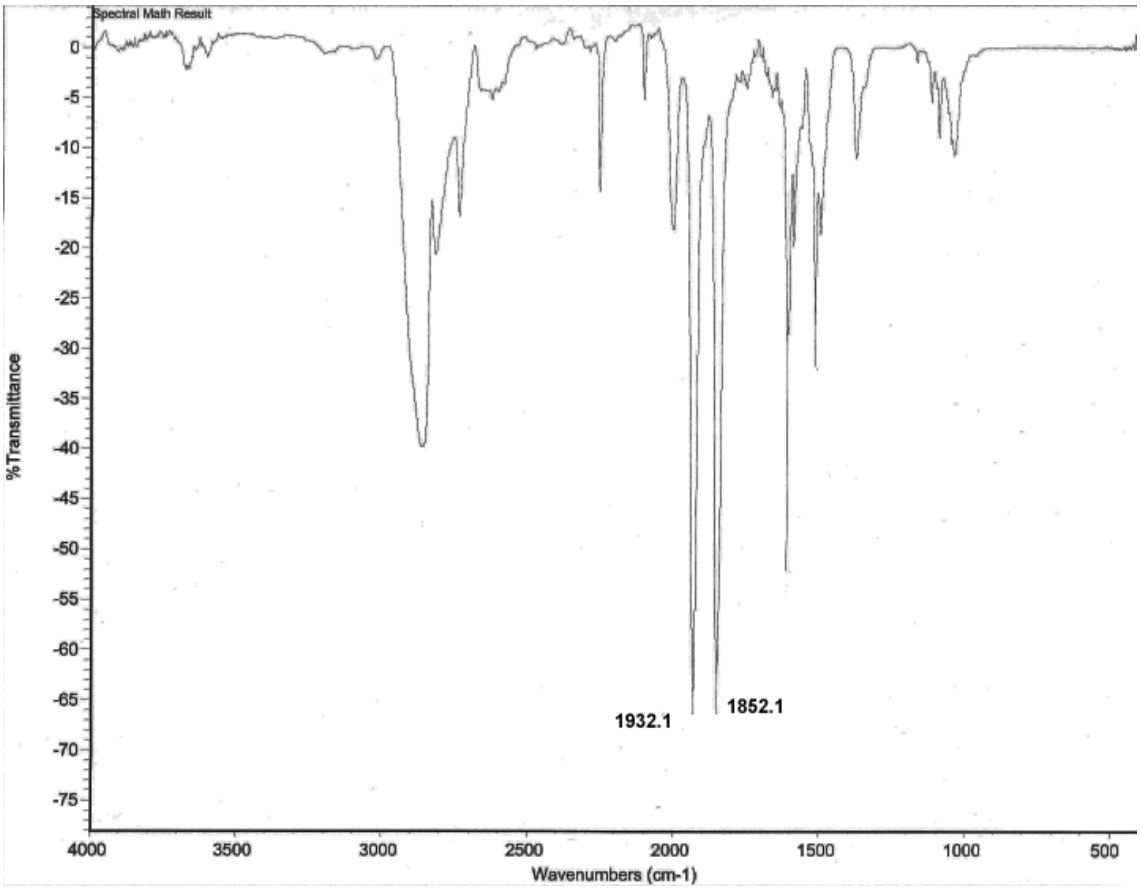

Figure B7. Solution IR (DCM) of ***p*-P_2ReCl$(CO)_2$**.

Cyclic Voltammograms

All scans were taken of 0.5 mM complex in THF with 0.1 M TBAP electrolyte using a glassy carbon electrode and Ag/Ag^+ reference electrode using dry solvents under N_2 atmosphere unless otherwise specified. Scan rate is 100 mV/sec unless stated otherwise.

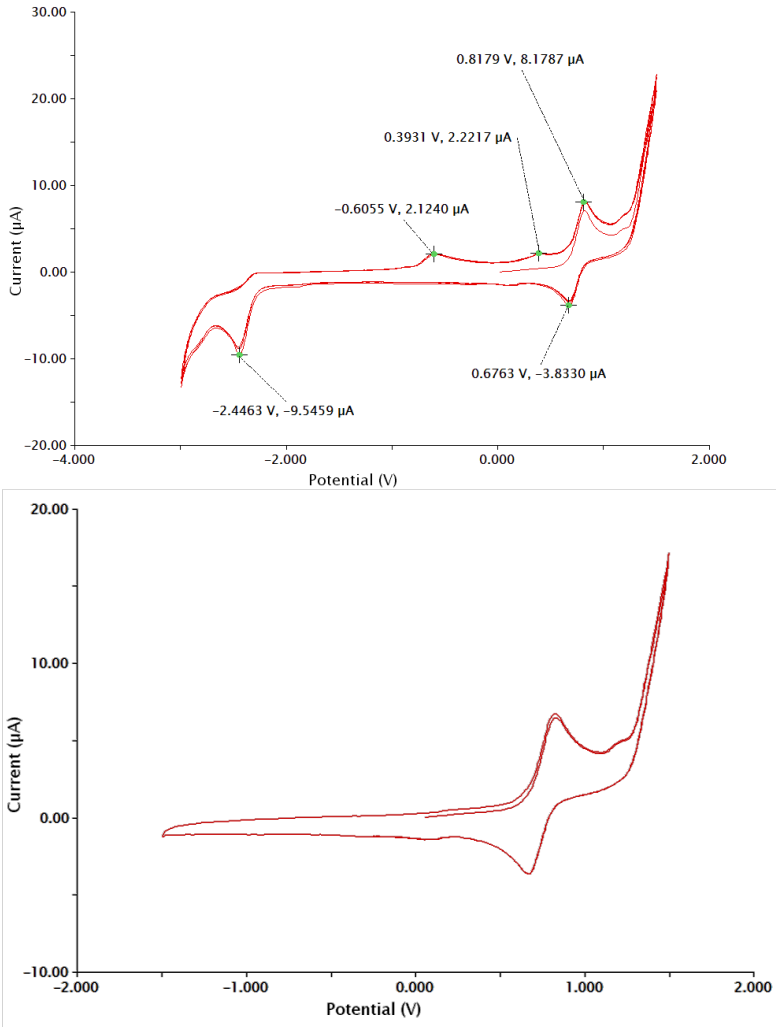

Figure B8. CV of ***m*-P$_2$ReCl(CO)$_2$** in THF at varying potential windows.

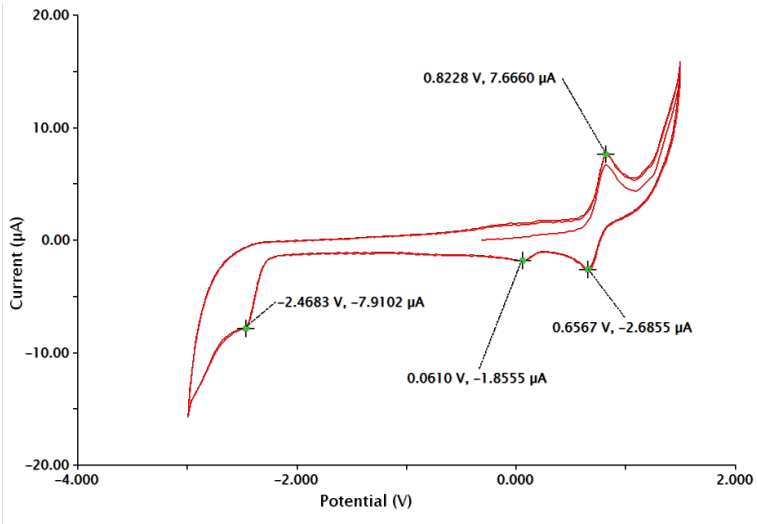

Figure B9. CV of ***m*-P$_2$ReCl(CO)$_2$** in THF under CO_2.

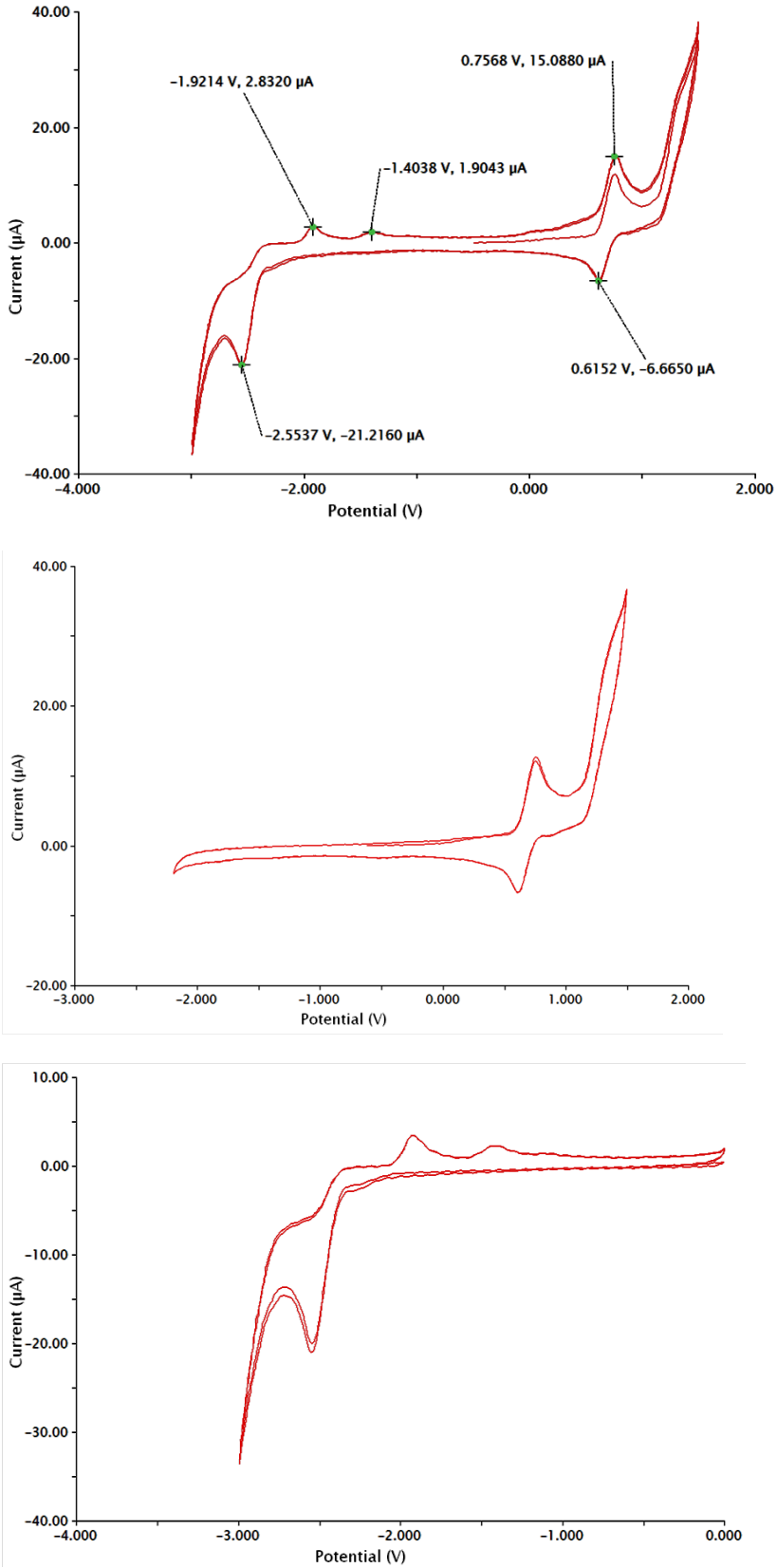

Figure B10. CV of ***p*-P$_2$ReCl(CO)$_2$** in THF at varying potential windows.

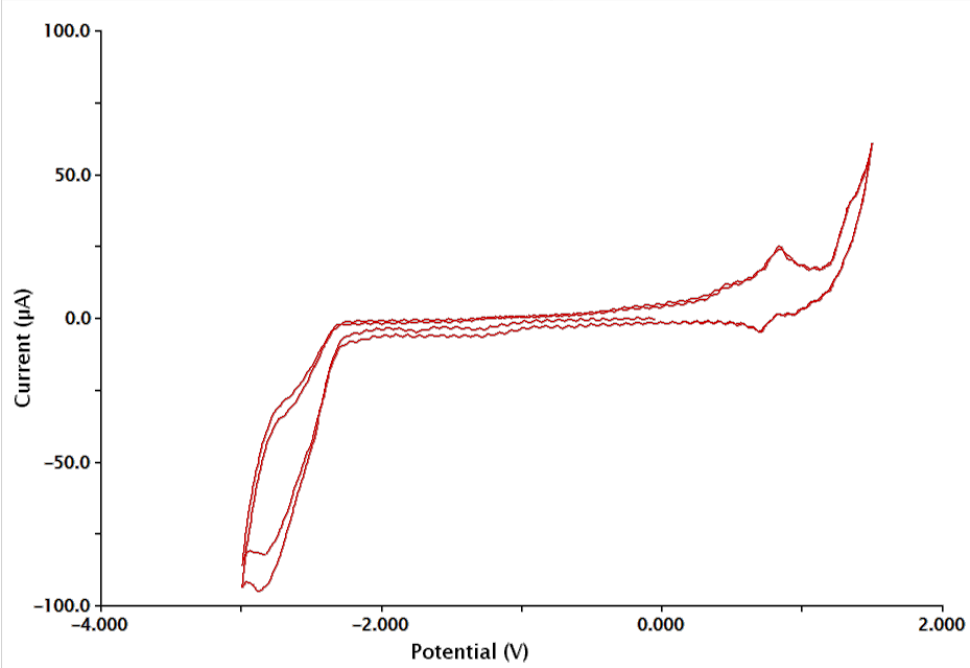

Figure B11. CV of ***p*-$P_2ReCl(CO)_2$** in THF under CO_2.

Crystallographic Data

Table B1. Structure of ***m*-$P_2ReCl(CO)_2$** (Preliminary structure).

Crystal system	monoclinic
Space group	P 1 21/c 1 (14)
Cell parameters	a=16.5810(21)Å b=34.4950(44)Å c=11.5451(15)Å ß=91.889(2)°
Cell ratio	a/b=0.4807 b/c=2.9878 c/a=0.6963
Cell volume	6599.77(146) $Å^3$

Atomic Parameters

Atom	x/a	y/b	z/c	U
Re1	0.13354	0.87223	0.11569	
Re2	0.63442	0.86748	0.57683	
P3	0.08752	0.81616	0.22576	
P4	0.19705	0.92294	0.00249	
Cl1	0.25014	0.83231	0.05893	
P6	0.69441	0.92344	0.48076	
C1	0.70735	0.90928	0.32917	
C7	0.48019	0.83248	0.43444	
C8	0.56881	0.8782	0.33814	
C9	0.41705	0.85891	0.42225	
H9	0.36575	0.8528	0.45169	-1.2
C13	0.49002	0.74088	0.61914	

H13	0.52041	0.7299	0.68216	-1.2
C2	0.77625	0.91678	0.26579	
H2	0.81813	0.93244	0.29887	-1.2
C3	0.64547	0.88659	0.2775	
C10	0.55681	0.8421	0.39217	
H10	0.6002	0.82422	0.40022	-1.2
C14	0.51162	0.77769	0.57662	
C15	0.46563	0.79343	0.4843	
C16	0.40032	0.77232	0.43443	
H16	0.36997	0.78284	0.37065	-1.2
C4	0.78425	0.90158	0.1548	
H4	0.83158	0.9068	0.11332	-1.2
C17	0.38024	0.73608	0.4785	
H17	0.33577	0.72211	0.44549	-1.2
C5	0.72328	0.87881	0.10449	
H5	0.72882	0.86825	0.02917	-1.2
C11	0.50331	0.90408	0.32443	
H11	0.51036	0.92814	0.28605	-1.2
C18	0.42517	0.72042	0.57055	
H18	0.41158	0.69569	0.60038	-1.2
C6	0.65388	0.87172	0.16635	
H6	0.6117	0.85651	0.13211	-1.2
C12	0.42882	0.89447	0.36678	
H12	0.38518	0.9122	0.35813	-1.2
C25	0.03008	0.77765	0.15053	
H25	0.07786	0.76768	0.10905	-1.2
C35	0.15458	0.87552	-0.18425	
C19	0.06998	0.83317	-0.0557	
H19	0.11591	0.81767	-0.03678	-1.2
C36	0.21131	0.9033	-0.14306	
C20	0.07868	0.86728	-0.1214	
C21	-0.00726	0.82186	-0.01762	
C26	0.0176	0.7424	0.21023	
H26	0.0469	0.73737	0.28073	-1.2
C31	0.27743	0.91147	-0.21153	
H31	0.31569	0.93037	-0.18588	-1.2
C27	-0.01507	0.78508	0.04814	
C33	0.23374	0.86402	-0.35377	
H33	0.24207	0.85017	-0.42349	-1.2
C22	-0.07425	0.84446	-0.04586	
H22	-0.12588	0.83709	-0.02015	-1.2
C32	0.28834	0.89245	-0.31664	
H32	0.33287	0.89888	-0.36267	-1.2

C23	0.00912	0.88982	-0.14945	
H23	0.01391	0.91288	-0.19368	-1.2
C28	-0.07142	0.75751	0.00673	
H28	-0.10252	0.76269	-0.06211	-1.2
C24	-0.0659	0.87819	-0.11232	
H24	-0.11225	0.89328	-0.13219	-1.2
C34	0.16645	0.85599	-0.28758	
H34	0.12853	0.837	-0.31359	-1.2
C29	-0.03745	0.7149	0.16644	
H29	-0.04417	0.69099	0.20576	-1.2
C30	-0.08225	0.72267	0.06533	
H30	-0.1203	0.70423	0.03611	-1.2
Cl2	0.74086	0.82929	0.48123	
P1	0.58521	0.80685	0.66191	
C38	0.54629	0.89684	0.62749	
O1	0.49288	0.91524	0.6533	
O3	-0.01594	0.92045	0.15684	
O2	0.2167	0.89824	0.34104	
C39	0.04011	0.90205	0.14263	
C40	0.18365	0.88915	0.25375	
C42	0.03982	0.85991	0.41919	
H42A	0.0336	0.88419	0.37574	-1.5
H42B	0.09642	0.85668	0.44449	-1.5
H42C	0.00593	0.86067	0.48711	-1.5
C41	0.01415	0.82595	0.34169	
H41	0.01234	0.80234	0.39177	-1.2
C44	0.20939	0.75737	0.23146	
H44A	0.26378	0.75098	0.26134	-1.5
H44B	0.21176	0.76504	0.1499	-1.5
H44C	0.17436	0.73465	0.23808	-1.5
C43	0.17522	0.7911	0.3023	
H43	0.21929	0.81089	0.30682	-1.2
C45	0.79633	0.94076	0.52993	
H45	0.81585	0.95886	0.4693	-1.2
C46	-0.0713	0.83236	0.28934	
H46A	-0.10883	0.8369	0.35174	-1.5
H46B	-0.08829	0.80933	0.24519	-1.5
H46C	-0.07122	0.85491	0.23774	-1.5
C47	0.16316	0.77842	0.42831	
H47A	0.12551	0.75653	0.42935	-1.5
H47B	0.14114	0.8001	0.47212	-1.5
H47C	0.21514	0.77055	0.46373	-1.5
C48	0.63237	0.9686	0.46457	

H48	0.58043	0.96029	0.42569	-1.2
C49	0.66128	0.76901	0.7092	
H49	0.63445	0.75211	0.76683	-1.2
C50	0.69343	0.87746	0.71343	
O4	0.73267	0.88319	0.79817	
C51	0.29915	0.94142	0.04493	
H51	0.31511	0.95974	-0.01739	-1.2
C53	0.36452	0.91	0.05302	
H53A	0.41777	0.92226	0.06027	-1.5
H53B	0.36164	0.89397	-0.01707	-1.5
H53C	0.35594	0.8937	0.12103	-1.5
C52	0.29941	0.96464	0.15742	
H52A	0.27952	0.94834	0.21986	-1.5
H52B	0.26434	0.98734	0.14732	-1.5
H52C	0.35452	0.97316	0.17732	-1.5
C54	0.13539	0.96751	-0.02716	
H54	0.08436	0.95839	-0.06692	-1.2
C55	0.17393	0.99593	-0.11129	
H55A	0.13386	1.01527	-0.13688	-1.5
H55B	0.19287	0.98171	-0.17866	-1.5
H55C	0.21968	1.00899	-0.07208	-1.5
C58	0.52315	0.81181	0.79438	
H58	0.51731	0.78529	0.82808	-1.2
C57	0.85765	0.90747	0.54134	
H57A	0.91211	0.9182	0.55211	-1.5
H57B	0.85491	0.89162	0.47089	-1.5
H57C	0.84505	0.89138	0.60831	-1.5
C56	0.79531	0.96338	0.64452	
H56A	0.76681	0.94824	0.70219	-1.5
H56B	0.76763	0.9882	0.63182	-1.5
H56C	0.85084	0.96815	0.67262	-1.5
C59	0.43799	0.82655	0.76275	
H59A	0.40792	0.83018	0.8336	-1.5
H59B	0.41	0.80757	0.7127	-1.5
H59C	0.44164	0.85133	0.72171	-1.5
C60	0.60883	0.98764	0.57887	
H60A	0.65184	1.0053	0.60558	-1.5
H60B	0.60106	0.96755	0.63746	-1.5
H60C	0.55856	1.00223	0.56649	-1.5
C63	0.68808	0.74245	0.61118	
H63A	0.72343	0.75688	0.56021	-1.5
H63B	0.64055	0.73332	0.56645	-1.5
H63C	0.71741	0.72017	0.64424	-1.5

C61	0.66834	0.99881	0.38383	
H61A	0.63133	1.02085	0.3754	-1.5
H61B	0.67639	0.98713	0.3077	-1.5
H61C	0.72029	1.00776	0.41675	-1.5
C62	0.73598	0.78648	0.77122	
H62A	0.7702	0.76558	0.80275	-1.5
H62B	0.71907	0.80324	0.83451	-1.5
H62C	0.76643	0.80177	0.71603	-1.5
C64	0.56215	0.83726	0.88797	
H64A	0.57036	0.86337	0.85711	-1.5
H64B	0.61432	0.82617	0.9128	-1.5
H64C	0.52692	0.83863	0.95436	-1.5
C65	0.1094	0.98918	0.08272	
H65A	0.15398	1.00548	0.11203	-1.5
H65B	0.09532	0.97032	0.14221	-1.5
H65C	0.06244	1.00549	0.06356	-1.5
C67	0.97275	0.00139	0.38514	
H67	0.95432	0.00225	0.30639	-1.2
C68	0.93977	0.02676	0.46568	
C69	1.0323	-0.02505	0.41946	
H69	1.05407	-0.04209	0.36392	-1.2
C70	0.87698	0.05623	0.42788	
H70A	0.84382	0.0629	0.49371	-1.5
H70B	0.84258	0.04531	0.3654	-1.5
H70C	0.90376	0.0796	0.39999	-1.5
C77	0.43822	0.01399	-0.07202	
H77	0.39612	0.02348	-0.12213	-1.2
C78	0.44445	0.02718	0.04111	
C79	0.50711	0.01305	0.1137	
H79	0.51246	0.02189	0.19151	-1.2
C80	0.38522	0.05655	0.08575	
H80A	0.39123	0.05824	0.17033	-1.5
H80B	0.33009	0.04846	0.06419	-1.5
H80C	0.39599	0.08197	0.05164	-1.5

Anisotropic displacement parameters (in $Å^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re1	0.0073	0.0101	0.00915	-0.00008	-0.00025	-0.00071
Re2	0.00751	0.01333	0.01051	-0.00073	-0.00083	-0.00034
P3	0.00923	0.01098	0.01106	-0.00123	0.00004	-0.0003
P4	0.01192	0.01212	0.01085	-0.00228	-0.00084	0.00031
Cl1	0.01214	0.0179	0.02134	0.00229	0.001	-0.00091

P6	0.01083	0.01331	0.01157	-0.00219	0.00037	-0.0015
C1	0.01286	0.01516	0.01041	-0.00122	-0.00042	-0.00222
C7	0.01066	0.01651	0.01293	-0.00148	0.00005	-0.00172
C8	0.01358	0.01631	0.01319	-0.00324	-0.00115	-0.00208
C9	0.00828	0.02072	0.01867	-0.00165	0	-0.00018
C13	0.01523	0.01794	0.02322	-0.00239	-0.0003	0.00224
C2	0.01365	0.01976	0.01488	-0.00323	0.00177	-0.00029
C3	0.01341	0.01637	0.01132	-0.00167	0.00089	-0.00043
C10	0.00888	0.01549	0.01434	-0.00142	-0.00031	-0.00016
C14	0.01279	0.01748	0.01746	-0.00284	0.00001	0.00232
C15	0.0106	0.01595	0.01594	-0.0022	0.00182	0.00008
C16	0.01216	0.02125	0.02005	-0.00327	-0.00024	-0.00148
C4	0.01481	0.02106	0.01447	-0.00129	0.00368	0.0005
C17	0.01558	0.01769	0.02206	-0.00489	0.00183	-0.00142
C5	0.01829	0.02336	0.01277	-0.00144	0.00143	-0.00314
C11	0.01367	0.0188	0.01511	-0.00126	-0.00288	0.00285
C18	0.01707	0.01677	0.02529	-0.00448	0.00367	0.00034
C6	0.01785	0.02235	0.01312	-0.00455	0.0009	-0.00251
C12	0.01224	0.01823	0.02	0.00213	-0.00318	-0.00016
C25	0.01033	0.01254	0.0129	-0.00212	0.00096	-0.00116
C35	0.01317	0.0148	0.00834	-0.00075	0.00008	0.00012
C19	0.01012	0.01388	0.01013	-0.00139	-0.00137	-0.00178
C36	0.01339	0.01416	0.01121	-0.00051	0.00036	0.00061
C20	0.01075	0.01485	0.01403	-0.00104	0.0002	-0.00118
C21	0.01004	0.01649	0.01146	-0.00086	-0.00103	-0.00189
C26	0.0144	0.01505	0.01926	-0.00298	0.00093	0.00038
C31	0.01303	0.02001	0.01222	-0.00258	0.00017	0.00124
C27	0.0096	0.01696	0.01399	-0.00225	0.00105	-0.00208
C33	0.01826	0.02253	0.01297	-0.00015	0.00267	-0.00341
C22	0.00814	0.02315	0.01647	-0.00067	-0.00092	-0.00048
C32	0.01544	0.02413	0.01301	0.00048	0.0032	0.00006
C23	0.01653	0.01576	0.01623	0.00107	-0.00089	-0.00011
C28	0.01353	0.0212	0.01444	-0.00441	0.00184	-0.00361
C24	0.01088	0.02268	0.01793	0.00283	-0.00259	0.00004
C34	0.01739	0.01659	0.01396	-0.00104	0.0003	-0.00165
C29	0.01818	0.01738	0.0184	-0.00567	0.00316	-0.00225
C30	0.01489	0.02027	0.02095	-0.00863	0.00334	-0.00358
Cl2	0.01279	0.02073	0.0228	0.00169	-0.00077	-0.00049
P1	0.0106	0.01591	0.01467	-0.0015	-0.00212	0.00234
C38	0.02371	0.02242	0.013	-0.01048	-0.00201	-0.00032
O1	0.02119	0.03028	0.03285	-0.00742	-0.00359	-0.00326
O3	0.02087	0.02559	0.0275	-0.00349	-0.0039	-0.00151
O2	0.0199	0.03327	0.01409	-0.01012	-0.00318	-0.00222

C39	0.02483	0.01598	0.01252	-0.00693	-0.00117	-0.00049
C40	0.01043	0.01682	0.01471	-0.00278	-0.00106	0.00021
C42	0.01609	0.02116	0.01621	-0.00199	0.00212	-0.00562
C41	0.01106	0.01718	0.01411	-0.00033	0.00263	-0.00004
C44	0.01872	0.01635	0.01731	0.00284	-0.0006	-0.00259
C43	0.01179	0.01453	0.01321	0.00003	-0.0018	-0.00045
C45	0.01439	0.01811	0.01546	-0.00435	0.00102	-0.00446
C46	0.01156	0.02379	0.01946	-0.00036	0.00136	-0.00242
C47	0.02042	0.02057	0.0141	0.00104	-0.00311	0.00361
C48	0.01829	0.01463	0.02005	0.00075	-0.00168	-0.00093
C49	0.01643	0.02014	0.02958	0.00135	-0.00401	0.00576
C50	0.01134	0.02125	0.0153	-0.00166	0.00023	-0.00056
O4	0.01504	0.0369	0.01583	-0.00538	-0.00483	-0.00096
C51	0.01454	0.01653	0.01561	-0.00462	-0.00268	0.0009
C53	0.01427	0.0253	0.02684	-0.00321	-0.00477	-0.00068
C52	0.02453	0.02617	0.0177	-0.00962	-0.00257	-0.005
C54	0.01932	0.01254	0.01624	-0.00077	-0.00173	-0.00074
C55	0.03237	0.01528	0.02298	-0.00125	-0.00141	0.00385
C58	0.01556	0.02193	0.01698	-0.00428	-0.00054	0.00342
C57	0.01252	0.02684	0.02367	0.00077	-0.00073	-0.00581
C56	0.02018	0.02632	0.0192	-0.00553	-0.00145	-0.00791
C59	0.01884	0.03609	0.02428	0.0045	0.00506	0.00842
C60	0.02835	0.02009	0.0236	0.00362	0.00372	-0.00419
C63	0.02027	0.01939	0.04919	0.002	0.00041	-0.00141
C61	0.04348	0.0197	0.02556	0.0015	0.00748	0.00513
C62	0.0201	0.03236	0.03981	0.00228	-0.01298	0.00593
C64	0.03294	0.04328	0.01958	-0.01817	0.0061	-0.00695
C65	0.02772	0.02036	0.02637	0.00248	0.00442	-0.00616
C67	0.02732	0.01957	0.01761	-0.00072	-0.00231	-0.00049
C68	0.02068	0.01737	0.01995	-0.00038	-0.00407	0.00061
C69	0.02368	0.02089	0.01971	0.00125	-0.00144	-0.00161
C70	0.0348	0.03159	0.02594	0.01265	-0.01006	-0.00265
C77	0.02436	0.02751	0.02669	-0.00433	0.00178	0.00127
C78	0.02685	0.02095	0.02836	-0.00206	0.00569	0.00023
C79	0.02803	0.028	0.02459	-0.00525	0.00137	0.00012
C80	0.03728	0.02713	0.03391	0.00373	0.0063	-0.00081

Atoms	**distance (Å)**	**Atoms**	**distance (Å)**

Re2-C10	2.6051(2)	Re1-C20	2.8610(3)
Re2-C7	3.2285(3)	Re1-C19	2.5892(2)
Re2-C8	2.9523(3)	Re1-C21	3.2560(3)

Table B2. Structure of ***p*-P$_2$ReBr(CO)$_2$** (Preliminary structure).

Crystal system	triclinic
Space group	P -1 (2)
Cell parameters	a=12.7407(13)Å b=15.6966(14)Å c=19.7465(18)Å α=77.397(5)° β=73.178(6)° γ=67.182(5)°
Cell ratio	a/b=0.8117 b/c=0.7949 c/a=1.5499
Cell volume	3458.99(59) Å^3

Atomic Parameters

Atom	x/a	y/b	z/c	U (Å^2)
Re1	0.40595	0.28759	0.43854	
Re2	0.10151	0.21544	0.07581	
Br1	0.59058	0.30434	0.34017	
Br2	0.21308	0.2127	0.17065	
P3	-0.07001	0.20005	0.17107	
P1	0.29932	0.31202	0.3437	
P2	0.51254	0.24804	0.5352	
C1	0.33254	0.46071	0.40936	
H1	0.37178	0.48472	0.36159	-1.2
C26	0.46448	0.15826	0.43084	
C2	0.21361	0.49407	0.54343	
H2	0.16952	0.50943	0.5897	-1.2
C17	0.38351	0.27537	0.25552	
H17	0.32721	0.27081	0.23136	-1.2
C7	0.15478	0.50121	0.36617	
C8	0.19873	0.43044	0.3203	
C18	0.43598	0.35062	0.20718	
H18A	0.49907	0.35151	0.22567	-1.5
H18B	0.37438	0.41214	0.20773	-1.5
H18C	0.46699	0.33482	0.15821	-1.5
C14	0.48395	0.33741	0.59292	
C3	0.21118	0.49139	0.42252	
C4	0.32671	0.45351	0.5348	
C15	0.54163	0.31478	0.64708	
H15	0.60165	0.2555	0.64941	-1.2
C23	0.35977	0.20182	0.66045	
H23A	0.30924	0.1642	0.67424	-1.5
H23B	0.31651	0.26496	0.64147	-1.5
H23C	0.38466	0.20453	0.70223	-1.5

C19	0.4824	0.18137	0.25538	
H19A	0.50856	0.16161	0.20767	-1.5
H19B	0.4544	0.1352	0.28984	-1.5
H19C	0.54782	0.18687	0.26853	-1.5
C20	0.20112	0.27902	0.35451	
H20	0.18575	0.28264	0.3069	-1.2
C5	0.15212	0.51675	0.48958	
H5	0.07013	0.54944	0.49934	-1.2
C6	0.3933	0.44067	0.46391	
H6	0.468	0.45378	0.45027	-1.2
C9	0.0633	0.57921	0.35286	
H9	0.03688	0.62917	0.38052	-1.2
C16	0.39163	0.42455	0.5906	
C24	0.46861	0.15722	0.60263	
H24	0.44352	0.12312	0.57663	-1.2
C10	0.00734	0.58693	0.29878	
H10	-0.06121	0.63922	0.29413	-1.2
C25	0.56448	0.08123	0.63961	
H25A	0.60543	0.11132	0.65622	-1.5
H25B	0.62058	0.03864	0.60542	-1.5
H25C	0.52743	0.04619	0.68032	-1.5
C22	0.07473	0.30314	0.41383	
H22A	0.03722	0.25892	0.41446	-1.5
H22B	0.02378	0.36656	0.40104	-1.5
H22C	0.08833	0.29821	0.46114	-1.5
C11	0.04991	0.51934	0.25118	
H11	0.01825	0.52664	0.21136	-1.2
C12	0.13972	0.44346	0.26756	
H12	0.16544	0.39346	0.24003	-1.2
C21	0.2357	0.14955	0.39963	
H21A	0.20709	0.14874	0.4514	-1.5
H21B	0.32037	0.1164	0.38828	-1.5
H21C	0.19688	0.11895	0.3817	-1.5
O1	0.50132	0.07854	0.43005	
C27	0.17104	0.04669	0.11683	
H27	0.18973	0.02953	0.16491	-1.2
C28	0.27535	0.03401	-0.00761	
C41	-0.01872	0.16893	0.30839	
H41A	0.06439	0.15671	0.28622	-1.5
H41B	-0.03517	0.11101	0.31663	-1.5
H41C	-0.03801	0.19295	0.35396	-1.5
C33	-0.01303	0.00248	0.16405	
C29	0.09009	0.00674	0.10676	

C44	-0.19267	0.23925	0.158	
H44	-0.24972	0.24269	0.20522	-1.2
C34	-0.07943	0.08002	0.20039	
C47	0.18715	0.32557	-0.09813	
H47	0.10461	0.36179	-0.07587	-1.2
C30	0.12408	-0.02237	0.03612	
H30	0.0811	-0.05491	0.02726	-1.2
C42	-0.08861	0.33598	0.25168	
H42A	-0.12036	0.35914	0.29832	-1.5
H42B	-0.1351	0.37794	0.21803	-1.5
H42C	-0.00728	0.33333	0.23412	-1.5
C31	0.21162	-0.00752	-0.01862	
H31	0.22593	-0.02695	-0.06377	-1.2
C35	-0.03881	-0.07609	0.18026	
H35	0.00539	-0.12672	0.153	-1.2
C38	0.35919	0.06224	-0.0644	
C39	0.45975	0.1743	-0.12551	
H39	0.46529	0.23401	-0.13003	-1.2
C32	0.25829	0.06447	0.06108	
H32	0.3314	0.05732	0.07453	-1.2
C43	-0.09325	0.24149	0.2586	
H43	-0.1759	0.2478	0.28337	-1.2
C36	-0.17134	0.07016	0.25743	
H36	-0.21829	0.12085	0.28423	-1.2
C40	0.37175	0.15212	-0.07372	
C37	-0.1943	-0.00875	0.27487	
H37	-0.25629	-0.01373	0.31434	-1.2
C45	-0.23456	0.19655	0.10491	
H45A	-0.17913	0.19209	0.05844	-1.5
H45B	-0.31267	0.23778	0.09873	-1.5
H45C	-0.23668	0.13452	0.12615	-1.5
C48	0.18079	0.2635	-0.14728	
H48A	0.11319	0.297	-0.16873	-1.5
H48B	0.1727	0.20578	-0.1191	-1.5
H48C	0.25249	0.24859	-0.185	-1.5
C65	0.34106	0.31081	-0.00901	
H65	0.38053	0.33253	-0.05758	-1.2
C46	-0.23089	0.35429	0.10686	
H46A	-0.18385	0.35023	0.05788	-1.5
H46B	-0.21531	0.39713	0.12882	-1.5
H46C	-0.31405	0.37733	0.1064	-1.5
C50	0.43606	0.25313	0.02768	
H50A	0.40497	0.25068	0.07936	-1.5

H50B	0.49764	0.28047	0.014	-1.5
H50C	0.46862	0.18998	0.01403	-1.5
C51	0.02861	0.34691	0.06981	
P4	0.25563	0.25017	-0.02348	
O2	-0.01546	0.42821	0.06821	
C52	0.72429	0.27634	0.48175	
H52A	0.69028	0.31224	0.44122	-1.5
H52B	0.80957	0.25051	0.46571	-1.5
H52C	0.70361	0.31713	0.51828	-1.5
C53	0.67866	0.20049	0.51165	
H53	0.70387	0.17331	0.55754	-1.2
C54	0.72514	0.12298	0.46704	
H54A	0.71847	0.14845	0.41791	-1.5
H54B	0.68009	0.0812	0.48598	-1.5
H54C	0.80748	0.08826	0.46785	-1.5
O3	0.20551	0.27423	0.54264	
C57	0.36464	0.47927	0.64263	
H57	0.30312	0.53776	0.64068	-1.2
C56	0.42179	0.45493	0.69895	
H56	0.39541	0.49345	0.73585	-1.2
O4	-0.0237	0.20875	-0.03036	
C58	0.52637	0.02384	-0.16782	
H58	0.57584	-0.01866	-0.20122	-1.2
C59	0.02461	0.21205	0.00115	
C60	0.24328	0.39733	-0.14231	
H60A	0.32842	0.36699	-0.15505	-1.5
H60B	0.22342	0.44797	-0.11416	-1.5
H60C	0.21368	0.42264	-0.18582	-1.5
C61	0.43423	0.00213	-0.11197	
H61	0.42596	-0.05638	-0.10847	-1.2
C62	0.54079	0.10993	-0.17135	
H62	0.60465	0.12372	-0.20442	-1.2
C63	0.26678	0.39768	0.02618	
H63A	0.228	0.3806	0.07503	-1.5
H63B	0.20765	0.43715	-0.00076	-1.5
H63C	0.31636	0.43181	0.02716	-1.5
C64	-0.13035	-0.0822	0.23703	
H64	-0.14855	-0.13767	0.24959	-1.2
O5	0.78359	0.16765	0.68488	
C68	0.86428	0.06829	0.67771	
H68A	0.82534	0.02772	0.67154	-1.2
H68B	0.90608	0.03995	0.71675	-1.2
C70	0.73704	0.2926	0.86513	

C71	0.85006	0.22773	0.6695	
H71A	0.88264	0.22347	0.71045	-1.2
H71B	0.80117	0.29324	0.65797	-1.2
C72	0.94662	0.10013	0.60288	
H72A	1.02675	0.05349	0.59657	-1.2
H72B	0.91483	0.1016	0.56227	-1.2
C73	0.95175	0.19055	0.60235	
H73A	0.93616	0.23134	0.5578	-1.2
H73B	1.02861	0.18546	0.60826	-1.2
C13	0.51947	0.37164	0.69911	0.0178
H13	0.56715	0.35516	0.73238	-1.2
C91	0.59312	0.32762	0.86357	0.0221

Anisotropic displacement parameters (in $Å^2$)

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Re1	0.02925	0.01134	0.01637	-0.00377	0.00171	-0.00358
Re2	0.03052	0.01157	0.01146	-0.00374	0.00119	-0.00512
Br1	0.02597	0.02655	0.03028	-0.00972	-0.00396	-0.00083
Br2	0.03009	0.02962	0.02878	-0.01135	-0.00157	-0.00727
P3	0.02298	0.0233	0.00251	-0.00875	0.00558	-0.00821
P1	0.02581	0.00378	0.00255	0.00333	0.00491	-0.0052
P2	0.02527	0.00931	0.03021	-0.00505	-0.0045	0.0038
C1	0.02083	0.00949	0.01673	0.0028	0.00522	0.00339
C26	0.04193	0.0144	0.01425	-0.00002	-0.00345	-0.01138
C2	0.02014	0.01971	0.02764	-0.00076	0.00532	-0.01045
C17	0.02121	0.02835	0.03541	-0.00067	-0.00892	-0.00537
C7	0.00517	0.02922	0.03032	-0.00728	-0.00275	0.00199
C8	0.01984	0.01668	0.0291	-0.00215	-0.00932	0.00297
C18	0.01922	0.04238	0.02645	-0.00936	-0.00122	0.01039
C14	0.02851	0.03123	0.02108	-0.02087	-0.00841	0.00227
C3	0.04256	0.01777	0.03366	-0.01688	-0.01697	0.00963
C4	0.02807	0.01758	0.02327	-0.00891	0.0016	-0.00225
C15	0.04735	0.01312	0.05496	-0.01184	-0.01638	0.00618
C23	0.03017	0.04206	0.03699	-0.00692	0.0136	-0.02758
C19	0.02908	0.02469	0.03889	-0.01137	-0.00291	-0.0167
C20	0.04101	0.31226	0.05517	0.0939	-0.03078	-0.17499
C5	0.03381	0.01153	0.0259	-0.00124	0.01341	-0.0142
C6	0.02308	0.01348	0.03745	-0.00646	-0.00769	-0.00595
C9	0.03021	0.02167	0.05559	-0.01007	-0.01852	0.00108
C16	0.01827	0.0276	0.02193	-0.00682	0.00149	-0.00004
C24	0.05592	0.02191	0.02602	-0.02453	-0.00035	0.00392
C10	0.02846	0.03209	0.04918	-0.01727	-0.00831	-0.00126

C25	0.07413	0.02531	0.04862	-0.0271	-0.02316	0.00657
C22	0.03318	0.00611	0.03898	-0.00279	0.00591	-0.01836
C11	0.01317	0.04739	0.03893	-0.00083	-0.00734	0.00382
C12	0.03837	0.02827	0.02546	-0.01282	0.00569	-0.01618
C21	0.0324	0.02664	0.05987	-0.02116	-0.00891	0.00025
O1	0.03826	0.00809	0.01718	0.00602	0.00309	-0.00946
C27	0.02713	0.01117	0.00834	0.00886	-0.00009	-0.00323
C28	0.02594	0.01501	0.01772	-0.00214	-0.0042	-0.00486
C41	0.02373	0.03126	0.01592	-0.00895	-0.00194	-0.00051
C33	0.0217	0.01952	0.03484	-0.01288	-0.00584	0.00075
C29	0.04227	0.01088	0.02201	-0.00704	-0.00665	-0.00145
C44	0.19002	0.06598	0.02083	-0.08305	0.07691	-0.07746
C34	0.02913	0.03632	0.01808	-0.01148	0.00132	-0.01158
C47	0.02121	0.04158	0.0202	0.01229	0.00941	-0.00132
C30	0.03126	0.01715	0.05214	0.01211	-0.0229	-0.02172
C42	0.05171	0.01343	0.03529	0.00494	-0.01554	-0.02014
C31	0.01979	0.03788	0.0277	-0.00732	-0.00831	0.00919
C35	0.04926	0.01644	0.02962	-0.01356	-0.01043	0.00185
C38	0.02188	0.02608	0.0201	0.00181	-0.005	-0.00716
C39	0.02806	0.00694	0.04542	-0.00062	-0.01058	-0.00018
C32	0.0172	0.02117	0.02861	-0.00038	-0.00425	0.00753
C43	0.02765	0.03273	0.03646	-0.01825	0.00555	-0.00345
C36	0.03294	0.01323	0.0292	-0.00901	-0.00359	-0.00081
C40	0.02191	0.01009	0.03256	0.00508	-0.00056	-0.01243
C37	0.02174	0.04591	0.029	-0.00271	0.00799	-0.01862
C45	0.02674	0.03805	0.02404	-0.00053	-0.00156	-0.00977
C48	0.04048	0.02604	0.02293	0.0113	0.00247	-0.00634
C65	0.01146	0.03221	0.03267	-0.00249	0.011	-0.00817
C46	0.00963	0.0272	0.08618	0.00739	-0.01065	-0.03781
C50	0.04935	0.10253	0.03374	-0.04468	-0.00664	-0.01112
C51	0.05231	0.01365	0.01303	-0.01004	-0.00234	0.0038
P4	0.02017	0.01675	0.03517	-0.00556	-0.00136	-0.00303
O2	0.06532	0.005	0.01882	-0.00955	0.00137	-0.00502
C52	0.02593	0.023	0.01059	0.00403	0.00884	-0.00581
C53	0.02007	0.01338	0.02965	0.00338	-0.00398	-0.00687
C54	0.03298	0.05031	0.03063	0.00501	-0.00492	-0.00811
O3	0.05932	0.02012	0.02469	-0.00451	-0.0277	-0.00694
C57	0.02575	0.02754	0.03285	-0.01096	-0.00071	-0.00075
C56	0.02886	0.0275	0.02875	-0.00764	0.0042	-0.00741
O4	0.03107	0.03238	0.01143	-0.00102	-0.01071	0.00705
C58	0.03286	0.03263	0.0254	-0.00026	-0.00364	-0.01982
C59	-0.00297	0.01407	-0.00297	0.00527	0.02084	0.00576
C60	0.02456	0.04072	0.04039	-0.00046	0.00028	0.02079

C61	0.06208	0.01677	0.03815	-0.01484	-0.0271	0.00872
C62	0.01148	0.08067	0.02307	-0.01794	-0.00542	0.01179
C63	0.02018	0.02376	0.07433	-0.01717	0.01308	-0.01081
C64	0.05951	0.031	0.03247	-0.01856	0.00007	-0.00144
O5	0.0468	0.06736	0.04508	-0.03675	0.01141	-0.00523
C68	0.02603	0.05922	0.07773	0.00159	0.00195	0.00805
C70	0.16171	0.21302	0.00037	0.17328	-0.01391	-0.03714
C71	0.06687	0.09997	0.07874	-0.04899	0.02009	-0.05995
C72	0.04843	0.1265	0.04486	0.01465	-0.00428	-0.00619
C73	0.04806	0.0303	0.07701	-0.00321	0.01332	-0.00901

Table B3. Structure of **[(*m*-$P_2(N(Me)_2)ORe(CO)_3$)]** (Preliminary structure).

Empirical formula	C35 H44 N O4 P2 Re	
Formula weight	790.85	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Unit cell dimensions	a = 11.9394(7) Å	a= 94.751(3)°.
	b = 14.8432(9) Å	b= 97.358(3)°.
	c = 18.7886(12) Å	g = 93.231(3)°.
Volume	3283.4(3) $Å^3$	
Z	4	
Density (calculated)	1.600 Mg/m^3	
Absorption coefficient	3.837 mm^{-1}	
F(000)	1592	
Crystal size	0.10 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.68 to 45.51°.	
Index ranges	-23<=h<=23, -29<=k<=29, -37<=l<=37	
Reflections collected	282633	
Independent reflections	54675 [R(int) = 0.0941]	
Completeness to theta = 45.51°	98.4 %	
Max. and min. transmission	0.7002 and 0.7002	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	54675 / 2 / 821	
Goodness-of-fit on F^2	0.965	
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.1041	
R indices (all data)	R1 = 0.0698, wR2 = 0.1101	
Largest diff. peak and hole	12.859 and -7.650 $e.Å^{-3}$	

Table B4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **[(*m*-P_2(N(Me)$_2$)ORe(CO)$_3$)]**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(8)	1667(2)	4670(1)	8750(1)	22(1)
C(1)	3293(2)	3121(1)	7813(1)	10(1)
C(2)	4236(2)	3742(1)	7802(1)	11(1)
C(3)	4972(2)	4023(2)	8430(1)	15(1)
C(4)	4805(2)	3713(2)	9092(1)	19(1)
C(5)	3892(2)	3075(2)	9093(1)	14(1)
C(6)	3158(2)	2753(1)	8469(1)	10(1)
C(7)	3815(2)	4373(1)	6569(1)	11(1)
C(8)	4543(2)	3996(1)	7097(1)	11(1)
C(9)	5637(2)	3822(2)	6954(1)	15(1)
C(10)	5992(2)	3947(2)	6290(1)	18(1)
C(11)	5240(2)	4238(2)	5753(1)	16(1)
C(12)	4171(2)	4460(1)	5895(1)	13(1)
C(13)	2379(2)	1939(1)	8509(1)	10(1)
C(14)	1272(2)	1706(1)	8149(1)	12(1)
C(15)	726(2)	877(2)	8267(1)	16(1)
C(16)	1218(2)	271(2)	8713(1)	15(1)
C(17)	2296(2)	495(1)	9068(1)	14(1)
C(18)	2851(2)	1306(1)	8962(1)	13(1)
C(19)	3081(2)	5738(1)	7549(1)	14(1)
C(20)	2180(2)	6386(2)	7723(1)	21(1)
C(21)	4202(2)	6259(2)	7493(1)	20(1)
C(22)	2011(2)	5437(2)	5983(1)	18(1)
C(23)	788(2)	5699(2)	5958(2)	24(1)
C(24)	2764(2)	6266(2)	5847(2)	22(1)
C(25)	-358(2)	1551(2)	6868(1)	18(1)
C(26)	-1332(2)	1920(2)	6390(1)	27(1)
C(27)	537(3)	1163(2)	6436(1)	26(1)
C(28)	-784(2)	2552(2)	8208(1)	16(1)
C(29)	-1634(2)	3240(2)	7971(2)	28(1)
C(30)	-268(2)	2845(2)	8981(1)	24(1)

C(31)	780(2)	3348(2)	6140(1)	18(1)
C(32)	-67(2)	4463(2)	7115(1)	17(1)
C(33)	1533(2)	4290(2)	8185(1)	15(1)
C(35)	8500(2)	9267(1)	7907(1)	10(1)
C(37)	8297(2)	9346(1)	8634(1)	10(1)
C(38)	8594(2)	8667(1)	9076(1)	12(1)
C(39)	9090(2)	7889(1)	8822(1)	12(1)
C(40)	9432(2)	7879(1)	8141(1)	12(1)
C(41)	9161(2)	8562(1)	7690(1)	11(1)
C(42)	9658(2)	8586(1)	7001(1)	10(1)
C(43)	9043(2)	8557(1)	6306(1)	11(1)
C(44)	9651(2)	8586(2)	5715(1)	16(1)
C(45)	10830(2)	8635(2)	5802(1)	19(1)
C(46)	11427(2)	8655(2)	6483(1)	18(1)
C(47)	10841(2)	8628(2)	7071(1)	14(1)
C(48)	7867(2)	10194(1)	8951(1)	10(1)
C(49)	8582(2)	10640(1)	9543(1)	13(1)
C(50)	8298(2)	11414(2)	9921(1)	16(1)
C(51)	7270(2)	11767(2)	9708(1)	18(1)
C(52)	6560(2)	11350(2)	9118(1)	16(1)
C(53)	6836(2)	10568(1)	8722(1)	11(1)
C(54)	7128(2)	8427(2)	5179(1)	16(1)
C(55)	7392(2)	9385(2)	4966(1)	23(1)
C(56)	5889(2)	8116(2)	4905(2)	28(1)
C(57)	7434(2)	7087(1)	6263(1)	14(1)
C(58)	6246(2)	6629(2)	6236(1)	19(1)
C(59)	8109(2)	6542(2)	5770(1)	21(1)
C(60)	4907(2)	10976(1)	7737(1)	15(1)
C(61)	3880(2)	10698(2)	7169(1)	22(1)
C(62)	5671(2)	11729(2)	7504(1)	22(1)
C(63)	4826(2)	9427(2)	8572(1)	15(1)
C(64)	3940(2)	8743(2)	8145(1)	21(1)
C(65)	5468(2)	8976(2)	9184(1)	23(1)
C(66)	8205(2)	6816(2)	9506(2)	27(1)
C(67)	9903(3)	6449(2)	9018(1)	25(1)
C(68)	5023(2)	8662(2)	6571(1)	14(1)

C(69)	6552(2)	8127(1)	7588(1)	11(1)
C(70)	6244(2)	10170(2)	6367(1)	16(1)
N(1)	9251(2)	7175(1)	9275(1)	15(1)
N(2A)	5440(6)	4112(7)	9728(2)	20(1)
C(34A)	6597(7)	4432(5)	9684(4)	19(1)
C(36A)	5304(13)	3666(12)	10429(8)	28(3)
N(2B)	5700(11)	3806(12)	9696(4)	19(3)
C(34B)	6670(20)	4438(19)	9658(14)	64(8)
C(36B)	5337(16)	3737(17)	10350(12)	12(2)
O(1)	2580(1)	2875(1)	7214(1)	10(1)
O(2)	8089(1)	9840(1)	7450(1)	10(1)
O(3)	495(2)	3201(2)	5549(1)	30(1)
O(4)	4139(1)	8355(1)	6296(1)	22(1)
O(5)	-841(2)	4910(2)	7075(1)	32(1)
O(6)	6549(1)	7502(1)	7911(1)	18(1)
O(7)	6042(2)	10708(1)	5980(1)	29(1)
P(1)	322(1)	2404(1)	7601(1)	11(1)
P(2)	2515(1)	4863(1)	6800(1)	11(1)
P(3)	7495(1)	8332(1)	6156(1)	10(1)
P(4)	5755(1)	10018(1)	8006(1)	10(1)
Re(1)	1203(1)	3743(1)	7181(1)	9(1)
Re(2)	6463(1)	9176(1)	7004(1)	9(1)

Table B5. Bond lengths [Å] and angles [°] for **[(*m*-P_2($N(Me)_2$)$ORe(CO)_3$)]**.

O(8)-C(33)	1.148(3)	C(4)-N(2B)	1.448(9)
C(1)-O(1)	1.333(2)	C(5)-C(6)	1.402(3)
C(1)-C(6)	1.414(3)	C(6)-C(13)	1.496(3)
C(1)-C(2)	1.417(3)	C(7)-C(12)	1.401(3)
C(2)-C(3)	1.396(3)	C(7)-C(8)	1.406(3)
C(2)-C(8)	1.492(3)	C(7)-P(2)	1.8363(19)
C(3)-C(4)	1.395(3)	C(8)-C(9)	1.400(3)
C(4)-N(2A)	1.398(4)	C(9)-C(10)	1.392(3)
C(4)-C(5)	1.403(3)	C(10)-C(11)	1.376(3)

C(11)-C(12)	1.389(3)	C(42)-C(43)	1.410(3)
C(13)-C(18)	1.411(3)	C(43)-C(44)	1.403(3)
C(13)-C(14)	1.417(3)	C(43)-P(3)	1.8410(19)
C(14)-C(15)	1.408(3)	C(44)-C(45)	1.393(3)
C(14)-P(1)	1.850(2)	C(45)-C(46)	1.381(3)
C(15)-C(16)	1.384(3)	C(46)-C(47)	1.384(3)
C(16)-C(17)	1.382(3)	C(48)-C(49)	1.407(3)
C(17)-C(18)	1.383(3)	C(48)-C(53)	1.411(3)
C(19)-C(21)	1.527(3)	C(49)-C(50)	1.382(3)
C(19)-C(20)	1.530(3)	C(50)-C(51)	1.387(3)
C(19)-P(2)	1.866(2)	C(51)-C(52)	1.385(3)
C(22)-C(23)	1.527(3)	C(52)-C(53)	1.404(3)
C(22)-C(24)	1.540(3)	C(53)-P(4)	1.843(2)
C(22)-P(2)	1.867(2)	C(54)-C(56)	1.534(3)
C(25)-C(26)	1.531(4)	C(54)-C(55)	1.536(4)
C(25)-C(27)	1.531(4)	C(54)-P(3)	1.851(2)
C(25)-P(1)	1.862(2)	C(57)-C(59)	1.518(3)
C(28)-C(30)	1.521(3)	C(57)-C(58)	1.531(3)
C(28)-C(29)	1.532(3)	C(57)-P(3)	1.874(2)
C(28)-P(1)	1.862(2)	C(60)-C(62)	1.531(3)
C(31)-O(3)	1.119(3)	C(60)-C(61)	1.531(3)
C(31)-Re(1)	1.986(2)	C(60)-P(4)	1.858(2)
C(32)-O(5)	1.166(3)	C(63)-C(64)	1.522(3)
C(32)-Re(1)	1.901(2)	C(63)-C(65)	1.524(3)
C(33)-Re(1)	1.973(2)	C(63)-P(4)	1.865(2)
C(35)-O(2)	1.328(2)	C(66)-N(1)	1.461(3)
C(35)-C(41)	1.411(3)	C(67)-N(1)	1.451(3)
C(35)-C(37)	1.413(3)	C(68)-O(4)	1.164(3)
C(37)-C(38)	1.392(3)	C(68)-Re(2)	1.895(2)
C(37)-C(48)	1.493(3)	C(69)-O(6)	1.150(3)
C(38)-C(39)	1.403(3)	C(69)-Re(2)	1.978(2)
C(39)-C(40)	1.391(3)	C(70)-O(7)	1.139(3)
C(39)-N(1)	1.419(3)	C(70)-Re(2)	1.983(2)
C(40)-C(41)	1.399(3)	N(2A)-C(34A)	1.451(10)
C(41)-C(42)	1.494(3)	N(2A)-C(36A)	1.543(17)
C(42)-C(47)	1.398(3)	N(2B)-C(36B)	1.36(2)

N(2B)-C(34B)	1.47(2)	C(18)-C(13)-C(6)	113.80(17)
O(1)-Re(1)	2.1436(14)	C(14)-C(13)-C(6)	129.72(17)
O(2)-Re(2)	2.1618(14)	C(15)-C(14)-C(13)	118.44(18)
P(1)-Re(1)	2.4326(5)	C(15)-C(14)-P(1)	112.16(15)
P(2)-Re(1)	2.4327(5)	C(13)-C(14)-P(1)	129.01(15)
P(3)-Re(2)	2.4441(5)	C(16)-C(15)-C(14)	123.5(2)
P(4)-Re(2)	2.4408(5)	C(17)-C(16)-C(15)	118.38(19)
		C(16)-C(17)-C(18)	119.27(19)
O(1)-C(1)-C(6)	121.48(17)	C(17)-C(18)-C(13)	123.98(19)
O(1)-C(1)-C(2)	120.52(16)	C(21)-C(19)-C(20)	111.05(18)
C(6)-C(1)-C(2)	117.97(17)	C(21)-C(19)-P(2)	117.66(15)
C(3)-C(2)-C(1)	121.05(18)	C(20)-C(19)-P(2)	111.38(16)
C(3)-C(2)-C(8)	118.94(17)	C(23)-C(22)-C(24)	109.1(2)
C(1)-C(2)-C(8)	119.42(17)	C(23)-C(22)-P(2)	113.28(16)
C(4)-C(3)-C(2)	121.58(19)	C(24)-C(22)-P(2)	115.34(17)
C(3)-C(4)-N(2A)	120.3(3)	C(26)-C(25)-C(27)	112.7(2)
C(3)-C(4)-C(5)	116.95(19)	C(26)-C(25)-P(1)	112.71(19)
N(2A)-C(4)-C(5)	122.3(2)	C(27)-C(25)-P(1)	110.16(17)
C(3)-C(4)-N(2B)	121.4(4)	C(30)-C(28)-C(29)	108.0(2)
N(2A)-C(4)-N(2B)	22.9(5)	C(30)-C(28)-P(1)	111.80(15)
C(5)-C(4)-N(2B)	118.9(4)	C(29)-C(28)-P(1)	113.39(16)
C(6)-C(5)-C(4)	123.08(19)	O(3)-C(31)-Re(1)	173.4(2)
C(5)-C(6)-C(1)	119.12(17)	O(5)-C(32)-Re(1)	179.5(2)
C(5)-C(6)-C(13)	117.66(17)	O(8)-C(33)-Re(1)	173.9(2)
C(1)-C(6)-C(13)	122.58(17)	O(2)-C(35)-C(41)	121.51(17)
C(12)-C(7)-C(8)	118.29(17)	O(2)-C(35)-C(37)	121.05(17)
C(12)-C(7)-P(2)	121.03(15)	C(41)-C(35)-C(37)	117.43(17)
C(8)-C(7)-P(2)	120.27(14)	C(38)-C(37)-C(35)	120.04(17)
C(9)-C(8)-C(7)	118.57(18)	C(38)-C(37)-C(48)	119.38(17)
C(9)-C(8)-C(2)	116.40(18)	C(35)-C(37)-C(48)	120.33(17)
C(7)-C(8)-C(2)	125.02(17)	C(37)-C(38)-C(39)	121.87(18)
C(10)-C(9)-C(8)	122.0(2)	C(40)-C(39)-C(38)	117.32(18)
C(11)-C(10)-C(9)	119.01(19)	C(40)-C(39)-N(1)	123.69(18)
C(10)-C(11)-C(12)	119.87(19)	C(38)-C(39)-N(1)	118.96(17)
C(11)-C(12)-C(7)	121.81(19)	C(39)-C(40)-C(41)	121.32(18)
C(18)-C(13)-C(14)	116.45(17)	C(40)-C(41)-C(35)	120.59(17)

C(40)-C(41)-C(42)	119.52(17)	O(7)-C(70)-Re(2)	174.9(2)
C(35)-C(41)-C(42)	119.69(17)	C(39)-N(1)-C(67)	115.94(18)
C(47)-C(42)-C(43)	118.82(17)	C(39)-N(1)-C(66)	113.53(18)
C(47)-C(42)-C(41)	115.34(17)	C(67)-N(1)-C(66)	111.1(2)
C(43)-C(42)-C(41)	125.83(16)	C(4)-N(2A)-C(34A)	116.9(5)
C(44)-C(43)-C(42)	118.22(17)	C(4)-N(2A)-C(36A)	117.3(7)
C(44)-C(43)-P(3)	119.94(15)	C(34A)-N(2A)-C(36A)	113.3(7)
C(42)-C(43)-P(3)	121.34(14)	C(36B)-N(2B)-C(4)	114.5(12)
C(45)-C(44)-C(43)	121.8(2)	C(36B)-N(2B)-C(34B)	118.1(14)
C(46)-C(45)-C(44)	119.74(19)	C(4)-N(2B)-C(34B)	117.5(12)
C(45)-C(46)-C(47)	119.22(19)	C(1)-O(1)-Re(1)	108.40(11)
C(46)-C(47)-C(42)	122.22(19)	C(35)-O(2)-Re(2)	102.49(11)
C(49)-C(48)-C(53)	118.50(18)	C(14)-P(1)-C(25)	101.70(10)
C(49)-C(48)-C(37)	114.69(17)	C(14)-P(1)-C(28)	99.29(9)
C(53)-C(48)-C(37)	126.80(17)	C(25)-P(1)-C(28)	103.87(11)
C(50)-C(49)-C(48)	122.5(2)	C(14)-P(1)-Re(1)	116.45(6)
C(49)-C(50)-C(51)	118.9(2)	C(25)-P(1)-Re(1)	114.35(7)
C(52)-C(51)-C(50)	119.7(2)	C(28)-P(1)-Re(1)	118.68(8)
C(51)-C(52)-C(53)	122.4(2)	C(7)-P(2)-C(19)	101.82(9)
C(52)-C(53)-C(48)	117.93(18)	C(7)-P(2)-C(22)	103.08(9)
C(52)-C(53)-P(4)	117.84(15)	C(19)-P(2)-C(22)	109.10(11)
C(48)-C(53)-P(4)	123.79(15)	C(7)-P(2)-Re(1)	112.35(6)
C(56)-C(54)-C(55)	109.9(2)	C(19)-P(2)-Re(1)	111.98(7)
C(56)-C(54)-P(3)	112.51(17)	C(22)-P(2)-Re(1)	117.11(8)
C(55)-C(54)-P(3)	112.81(17)	C(43)-P(3)-C(54)	103.43(9)
C(59)-C(57)-C(58)	110.11(19)	C(43)-P(3)-C(57)	98.44(9)
C(59)-C(57)-P(3)	114.31(16)	C(54)-P(3)-C(57)	105.63(10)
C(58)-C(57)-P(3)	115.56(15)	C(43)-P(3)-Re(2)	115.30(6)
C(62)-C(60)-C(61)	111.9(2)	C(54)-P(3)-Re(2)	119.05(7)
C(62)-C(60)-P(4)	110.10(15)	C(57)-P(3)-Re(2)	112.55(7)
C(61)-C(60)-P(4)	114.04(16)	C(53)-P(4)-C(60)	102.63(10)
C(64)-C(63)-C(65)	109.2(2)	C(53)-P(4)-C(63)	99.39(9)
C(64)-C(63)-P(4)	114.05(16)	C(60)-P(4)-C(63)	101.95(10)
C(65)-C(63)-P(4)	114.07(15)	C(53)-P(4)-Re(2)	116.10(6)
O(4)-C(68)-Re(2)	178.9(2)	C(60)-P(4)-Re(2)	113.96(7)
O(6)-C(69)-Re(2)	176.43(18)	C(63)-P(4)-Re(2)	120.18(7)

C(32)-Re(1)-C(33)	85.45(10)	C(68)-Re(2)-C(70)	87.54(10)
C(32)-Re(1)-C(31)	87.84(10)	C(69)-Re(2)-C(70)	174.70(9)
C(33)-Re(1)-C(31)	172.24(9)	C(68)-Re(2)-O(2)	175.95(8)
C(32)-Re(1)-O(1)	176.82(8)	C(69)-Re(2)-O(2)	96.84(7)
C(33)-Re(1)-O(1)	97.23(7)	C(70)-Re(2)-O(2)	88.42(8)
C(31)-Re(1)-O(1)	89.59(8)	C(68)-Re(2)-P(4)	95.16(6)
C(32)-Re(1)-P(1)	98.58(7)	C(69)-Re(2)-P(4)	87.96(6)
C(33)-Re(1)-P(1)	89.71(6)	C(70)-Re(2)-P(4)	93.19(7)
C(31)-Re(1)-P(1)	95.16(6)	O(2)-Re(2)-P(4)	84.98(4)
O(1)-Re(1)-P(1)	79.78(4)	C(68)-Re(2)-P(3)	94.25(6)
C(32)-Re(1)-P(2)	96.14(7)	C(69)-Re(2)-P(3)	87.60(6)
C(33)-Re(1)-P(2)	90.52(6)	C(70)-Re(2)-P(3)	92.12(7)
C(31)-Re(1)-P(2)	86.31(6)	O(2)-Re(2)-P(3)	85.98(4)
O(1)-Re(1)-P(2)	85.56(4)	P(4)-Re(2)-P(3)	169.376(18)
P(1)-Re(1)-P(2)	165.253(18)		
C(68)-Re(2)-C(69)	87.20(9)		

Table B6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **[(*m*-P_2(N(Me)$_2$)ORe(CO)$_3$)]**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(8)	25(1)	24(1)	17(1)	-4(1)	6(1)	-4(1)
C(1)	9(1)	9(1)	12(1)	2(1)	2(1)	0(1)
C(2)	9(1)	12(1)	13(1)	3(1)	2(1)	0(1)
C(3)	12(1)	16(1)	17(1)	2(1)	1(1)	-4(1)
C(4)	17(1)	24(1)	14(1)	2(1)	0(1)	-9(1)
C(5)	14(1)	18(1)	11(1)	2(1)	2(1)	-2(1)
C(6)	10(1)	11(1)	11(1)	3(1)	3(1)	-1(1)
C(7)	9(1)	11(1)	14(1)	2(1)	4(1)	0(1)
C(8)	9(1)	12(1)	15(1)	4(1)	4(1)	0(1)
C(9)	10(1)	16(1)	21(1)	6(1)	5(1)	3(1)
C(10)	14(1)	18(1)	25(1)	6(1)	10(1)	4(1)
C(11)	15(1)	17(1)	18(1)	2(1)	8(1)	-1(1)
C(12)	13(1)	14(1)	15(1)	3(1)	5(1)	1(1)
C(13)	10(1)	10(1)	11(1)	2(1)	4(1)	0(1)
C(14)	10(1)	11(1)	14(1)	3(1)	2(1)	-1(1)
C(15)	12(1)	14(1)	22(1)	5(1)	2(1)	-3(1)
C(16)	14(1)	13(1)	20(1)	5(1)	4(1)	-1(1)
C(17)	14(1)	13(1)	15(1)	5(1)	6(1)	2(1)
C(18)	11(1)	16(1)	12(1)	4(1)	3(1)	0(1)
C(19)	14(1)	11(1)	19(1)	1(1)	8(1)	0(1)
C(20)	20(1)	14(1)	31(1)	-1(1)	12(1)	2(1)
C(21)	18(1)	14(1)	28(1)	-1(1)	9(1)	-5(1)
C(22)	15(1)	20(1)	21(1)	11(1)	6(1)	4(1)
C(23)	17(1)	30(1)	30(1)	16(1)	6(1)	9(1)
C(24)	22(1)	20(1)	28(1)	11(1)	8(1)	2(1)
C(25)	21(1)	18(1)	15(1)	2(1)	1(1)	-8(1)
C(26)	19(1)	42(2)	17(1)	6(1)	-4(1)	-10(1)
C(27)	41(2)	17(1)	19(1)	-2(1)	5(1)	2(1)
C(28)	11(1)	21(1)	16(1)	5(1)	5(1)	0(1)
C(29)	18(1)	38(2)	34(1)	16(1)	12(1)	13(1)
C(30)	23(1)	33(1)	17(1)	2(1)	9(1)	-2(1)

C(31)	11(1)	15(1)	26(1)	5(1)	2(1)	-2(1)
C(32)	13(1)	18(1)	23(1)	8(1)	6(1)	4(1)
C(33)	12(1)	14(1)	19(1)	4(1)	4(1)	-2(1)
C(35)	7(1)	12(1)	11(1)	1(1)	2(1)	0(1)
C(37)	8(1)	11(1)	11(1)	0(1)	3(1)	0(1)
C(38)	11(1)	14(1)	12(1)	2(1)	3(1)	0(1)
C(39)	11(1)	13(1)	12(1)	2(1)	1(1)	2(1)
C(40)	10(1)	14(1)	13(1)	1(1)	2(1)	2(1)
C(41)	6(1)	14(1)	11(1)	1(1)	2(1)	2(1)
C(42)	7(1)	12(1)	12(1)	1(1)	3(1)	1(1)
C(43)	8(1)	12(1)	13(1)	1(1)	3(1)	0(1)
C(44)	12(1)	22(1)	13(1)	0(1)	5(1)	0(1)
C(45)	13(1)	26(1)	17(1)	-2(1)	8(1)	-2(1)
C(46)	8(1)	24(1)	20(1)	-1(1)	6(1)	0(1)
C(47)	8(1)	21(1)	14(1)	0(1)	3(1)	2(1)
C(48)	9(1)	11(1)	11(1)	1(1)	3(1)	-1(1)
C(49)	12(1)	14(1)	14(1)	1(1)	2(1)	0(1)
C(50)	18(1)	15(1)	15(1)	-2(1)	1(1)	-2(1)
C(51)	19(1)	14(1)	20(1)	-4(1)	3(1)	2(1)
C(52)	13(1)	13(1)	21(1)	-3(1)	2(1)	2(1)
C(53)	10(1)	10(1)	14(1)	0(1)	3(1)	0(1)
C(54)	14(1)	21(1)	13(1)	2(1)	0(1)	4(1)
C(55)	28(1)	25(1)	20(1)	9(1)	6(1)	6(1)
C(56)	19(1)	40(2)	23(1)	3(1)	-6(1)	2(1)
C(57)	12(1)	13(1)	18(1)	0(1)	4(1)	0(1)
C(58)	14(1)	16(1)	26(1)	-3(1)	5(1)	-3(1)
C(59)	19(1)	18(1)	28(1)	-1(1)	8(1)	6(1)
C(60)	13(1)	13(1)	20(1)	0(1)	3(1)	5(1)
C(61)	15(1)	22(1)	27(1)	1(1)	-2(1)	7(1)
C(62)	24(1)	14(1)	28(1)	4(1)	6(1)	4(1)
C(63)	12(1)	14(1)	18(1)	1(1)	5(1)	-1(1)
C(64)	15(1)	20(1)	26(1)	1(1)	4(1)	-7(1)
C(65)	19(1)	29(1)	22(1)	11(1)	3(1)	-2(1)
C(66)	22(1)	27(1)	34(1)	17(1)	5(1)	-1(1)
C(67)	37(1)	19(1)	24(1)	8(1)	8(1)	14(1)
C(68)	8(1)	17(1)	17(1)	-2(1)	2(1)	2(1)

C(69)	9(1)	11(1)	15(1)	-2(1)	4(1)	0(1)
C(70)	14(1)	17(1)	18(1)	3(1)	2(1)	5(1)
N(1)	17(1)	14(1)	16(1)	5(1)	4(1)	4(1)
N(2A)	19(2)	22(3)	17(1)	2(1)	-3(1)	-5(2)
C(34A)	16(2)	23(2)	14(2)	0(2)	-5(2)	-6(2)
C(36A)	40(4)	34(4)	10(4)	7(2)	1(2)	-2(3)
N(2B)	18(3)	20(5)	16(3)	2(2)	-5(2)	-6(3)
C(34B)	37(9)	84(15)	62(12)	24(10)	-11(8)	-46(9)
C(36B)	16(4)	18(4)	2(4)	3(3)	-1(2)	-5(3)
O(1)	8(1)	11(1)	11(1)	2(1)	1(1)	1(1)
O(2)	8(1)	11(1)	12(1)	2(1)	2(1)	0(1)
O(3)	37(1)	32(1)	20(1)	6(1)	5(1)	-3(1)
O(4)	9(1)	27(1)	28(1)	-6(1)	1(1)	-2(1)
O(5)	21(1)	36(1)	48(1)	24(1)	17(1)	17(1)
O(6)	17(1)	14(1)	22(1)	5(1)	3(1)	-1(1)
O(7)	34(1)	27(1)	30(1)	13(1)	6(1)	16(1)
P(1)	8(1)	13(1)	11(1)	3(1)	1(1)	-2(1)
P(2)	9(1)	10(1)	14(1)	3(1)	4(1)	1(1)
P(3)	7(1)	12(1)	11(1)	0(1)	2(1)	1(1)
P(4)	7(1)	10(1)	14(1)	0(1)	3(1)	1(1)
Re(1)	7(1)	11(1)	10(1)	3(1)	2(1)	0(1)
Re(2)	6(1)	9(1)	12(1)	0(1)	2(1)	1(1)

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